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# **OU 3-14 Tank Farm Alluvium Geochemical Properties Report**

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# **OU 3-14 Tank Farm Alluvium Geochemical Properties Report**

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## **ABSTRACT**

In 1972, 15,000 Ci of Sr-90 in 18,600 gal of sodium-bearing waste leaked into surficial alluvium in the tank farm at the Idaho Nuclear Technology and Engineering Center. The release of radionuclides is being evaluated to determine if the Sr-90 poses a risk to the Snake River Plain Aquifer. Because the liquid waste was very acidic and had a high ionic strength, the chemistry of the pore water in the alluvium underwent extreme changes in response to the leak. The traditional use of a reversible, equilibrium  $K_d$  value for Sr-90 transport is not valid under those conditions, and a competitive cation exchange model was identified as a more appropriate approach. To implement the cation exchange model, data were needed on (1) cation exchange capacity of alluvium, (2) pore water chemistry in alluvium, (3) chemistry of the release, and (4) selectivity coefficients for cation exchange in the alluvium. Existing characterization reports, some dating back to the 1950s, contained appreciable data on cation exchange capacity. These data are in good agreement and indicate a low cation exchange capacity (between 1.5 and 4.5 meq/100 g) for the alluvium. Pore water chemistry was estimated from measurements on vadose zone water chemistry in perched water. The chemistry of the release was obtained from company documents prepared when the release was discovered in 1975. Selectivity coefficients were taken from published values in the literature. The applicability of the selectivity coefficients was evaluated by comparing simulated strontium partitioning in the alluvium to laboratory experimental data. The literature values did a very good job of matching the laboratory experimental data. Review of existing data shows that sufficient geochemical information representative of the alluvium at the Idaho Nuclear Technology and Engineering Center is available to implement the competitive cation exchange model of the leak.



## EXECUTIVE SUMMARY

The objective of this report is to assess available data for parameters needed to implement a competitive cation exchange, reactive transport simulation, of Sr-90 migration through the alluvium at the Idaho Nuclear Technology and Engineering Center (INTEC) tank farm. Because of the dynamic chemical evolution of the pore water chemistry following the leak of sodium-bearing waste at CPP-31, a constant  $K_d$  approach to reactive transport cannot provide an accurate assessment of the fate of Sr-90 in the alluvium. In this report, existing data on geochemical transport parameters and environment are gathered and reviewed for representativeness and comparability to support a simulation of tank farm alluvium. Sensitivity of the predicted Sr-90 migration to the parameters is evaluated, and a recommendation provided regarding the suitability of the existing data set or the need to gather additional data.

Parameters and environmental conditions that will control the competitive cation exchange model are

- Cation exchange capacity
- Selectivity coefficients for cation exchange
- Composition of the exchange assemblage on the sediment
- Water chemistry of the pore water, infiltration, and sodium-bearing waste leak.

Available data for each of these areas are presented and discussed. Representativeness relative to the INTEC tank farm alluvium is assessed.

Cation exchange capacity arises from lattice substitutions within clay minerals giving rise to an excess negative charge at the clay surface. Cations are adsorbed to the clay surface through formation of outer-sphere complexes. Big Lost River alluvium around INTEC is coarse grained and low in clay minerals. Thus, cation exchange capacity (CEC) is expected to be low. CEC has been measured for sediments near INTEC by the United States Geological Survey (USGS) in 1956, by the Department of Energy (DOE) in 1965, and by the remediation program in the early 2000s. One significant issue with determination of CEC is that samples are frequently sieved before analysis to remove coarse material (generally  $> 2$  mm). If the mass of material is not recorded and the CEC value adjusted accordingly, the final measurement will be biased high. Because the fraction of material in alluvium  $> 2$  mm can be as high as 80%, the bias could be significant. USGS data from 1956 were adjusted to total sample mass, giving numbers representative of alluvium. The DOE data contained enough information to determine the initial sample mass, so that the measured CEC values could be corrected. CEC data collected for the ecological risk project have no associated grain-size measurements. A correction for grain size bias can be estimated but leaves a large uncertainty. USGS and DOE CEC values of alluvium range from 1.8 meq/100 g to 4.5 meq/100 g, with less reliable numbers from the ecological risk study as high as 20 meq/100 g (without adjustment).

Selectivity coefficients for cations depend mainly on the chemical properties of the cation and much less on the properties of the solid. Published series of cation selectivity show very good agreement, indicating that these numbers probably vary little. In 1965, Hawkins and Short (in *Equations for the Sorption of Cesium and Strontium on Soil and Clinoptilolite*, IDO-12046) measured strontium adsorption to Big Lost River alluvial sediments as a function of competing cation concentrations. They also measured the CEC of the sediments tested. Using selectivity coefficients from the literature, the Hawkins and Short experiments were simulated. The match between the simulations and the

experimental measurements were excellent for strontium. Selectivity coefficients from literature sources were adopted for the simulations.

Perched water samples collected as part of a geochemical investigation at INTEC were used to develop pore water chemistry. Perched water is saturated with respect to calcite at a partial pressure of carbon dioxide gas of 0.01 atm. This was adopted for pore water and fixes the calcium, inorganic carbon, and pH of the pore water. Sodium and chloride were added to the water at a concentration equal to water in the Snake River Plain Aquifer. The composition of the sodium-bearing waste was taken from Westinghouse Idaho Nuclear Company reports. Knowledge of the sodium-bearing waste composition is based on process knowledge and measurement of tank contents.

The composition of the initial exchange assemblage on cation exchange sites in the alluvium is not known. It is also not an independent variable, as the pore water and the exchange sites must be in equilibrium. The selectivity coefficients define this equilibrium. Thus, given the pore water chemistry adopted and the selectivity coefficients that were validated using the Hawkins and Short data, the in situ cation exchange assemblage was calculated. The resulting values compare well to measured distributions from the Subsurface Disposal Area.

Assessment of the existing data indicated availability of estimates for all geochemical parameters and environmental conditions. Next, the sensitivity of Sr-90 migration to the variables was assessed. The measures used to assess sensitivity are the curies of Sr-90 released to underlying basalt after 20 years and the calculated partitioning of Sr-90 ( $K_d$ ) between pore water and alluvium at 20 years.

Table ES-1. Results of sensitivity simulations to evaluate the effect of parameter uncertainty. All Sr-90 activities are undecayed.

Performance Measure	Parameter						
Activity Leaving Alluvium (years after release)	CEC=7 <sup>a</sup> (meq/100 g)	CEC=15 (meq/100 g)	CEC=5 (meq/100 g)	CEC=2 (meq/100 g)	$K_{Na/Sr}=0.25$	$K_{Na/Sr}=0.45$	$Na^+ = 0.22$ mmol/L
5	1,773	349	2,793	5,187	1,658	3,090	1,921
10	6,378	1,715	8,352	12,272	3,369	9,454	6,497
15	6,393	1,725	8,368	12,310	3,373	9,470	6,509
20	6,403	1,731	8,380	12,336	3,378	9,480	6,517
$K_d$ range (mL/g) (at 20 yr)	7–30	20–50	4–18	1.5–4	15–50	7–15	10–35

a. Base case: CEC = 7 meq/100 g;  $Na^+ = 0.33$  mmol/L;  $K_{Na/Sr} = 0.35$ .

Parameters assessed for sensitivity were CEC, the sodium-strontium selectivity coefficient, and the sodium concentration of pore water. The simulations showed little sensitivity to the pore-water sodium concentration. Sensitivity to the sodium-strontium exchange coefficient was moderate but well constrained. Refining the selectivity coefficients would require significant effort and is not likely to result in a significant change in values. The impact on the assessed risk is small. Sr-90 mobility is very sensitive to the CEC. At the lowest CEC used in the sensitivity study (2 meq/100 g), 12,000 Ci of Sr-90 were released in 10 years compared to 6,400 Ci released in the base case (7 meq/100 g). This range is within the observed range of existing data, although the most reliable data (1956 USGS data and 1965 Hawkins and Short data) are toward the lower end of this range (2 to 4.5 meq/100 g). Additional CEC data collected from surficial alluvium are likely to fall within the range of reliable existing values and are not likely to refine the estimate of Sr-90 curies released to underlying basalt from the alluvium.

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# **OU 3-14 Tank Farm Alluvium Geochemical Properties Report**

## **1. INTRODUCTION**

### **1.1 Problem**

In 1972, 15,000 Ci of Sr-90 in 18,600 gal of sodium-bearing waste was released to surficial alluvium in the tank farm at the Idaho Nuclear Technology and Engineering Center (INTEC). This highly acidic, very high ionic strength sodium-bearing waste from the concentrate of the Process Equipment Waste Evaporator is responsible for the majority of contaminants currently in the alluvium and underlying vadose zone at INTEC. Released radionuclides are currently being investigated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) process and are the primary focus of the remedial investigation/baseline risk assessment/feasibility study (RI/BRA/FS). Previous efforts to evaluate the fate of this Sr-90 have used numerical models with a constant  $K_d$  parameter to simulate reactive transport. The use of  $K_d$  values to simulate sorption is only strictly valid in a system that is at complete steady state from a geochemical perspective (Reardon 1981). In the case of the acidic sodium-bearing waste release at the INTEC tank farm, the chemistry of the pore water in the vadose zone underwent extreme changes in chemistry. To address the highly dynamic evolution of the released fluid as it was transported through the vadose zone, a more robust approach was needed and is presented in this report.

### **1.2 Geochemical Processes Overview**

A geochemical conceptual model was used to identify the important system components and processes that will alter/control the transport of strontium resulting from the CPP-31 release. The processes considered to be important are based on the high ionic strength of the acidic sodium-bearing waste. First, minerals will be dissolved by the strong acid in the sodium-bearing waste, consuming hydrogen ion from the released solution, which will result in an increase of the pH of the acidic solution and decrease in pH of the native pore water. As the pH of the acidic fluid rises, the solution may become supersaturated with other minerals that will precipitate. Second, the high concentration of cations released in the sodium-bearing waste, and generated by dissolution of minerals, will compete for exchange sites on clay minerals in the sediment. The complex interaction between dissolved mineral species and competition for exchange sites ultimately dictates the evolution of the individual solution species. To develop a quantitative representation of this system, consideration must be given to the alluvial sediments, chemistry of the native pore water and infiltrating solution, and the background hydrologic system, including natural recharge. A general overview of the interactions between solid and aqueous phases is discussed below, with details of the geochemical model presented in the following section.

The alluvial sediment is a mixture of quartz, calcite, alumino-silicate minerals, and clays. The reaction of calcite with the initial sodium-bearing waste will release carbon dioxide gas into the pore space of the unsaturated alluvium and will release calcium into the pore water. This dissolution of calcite will occur rapidly in strong acid, allowing use of an equilibrium model for this process. Alumino-silicate minerals will dissolve more slowly, and, if the pH is rapidly neutralized by the calcite, these minerals can be considered inert. However, as the pH of the sodium-bearing waste increases, the solubility of individual sodium-bearing waste components will change. Of particular interest is the aluminum, which is a major component of the sodium-bearing waste (0.5 M). The precipitation of aluminum as gibbsite, or its inclusion in secondary clay minerals, may play a role in buffering the pH. Buffering the pH of the pore water will, in turn, alter the concentrations of competing species. In contrast, even though the activity of

the individual radionuclides is elevated in the sodium-bearing waste, the molal quantities of the radionuclides are low. As a result, the radionuclide mobility will most likely be controlled by sorption to mineral surfaces as opposed to being controlled by the precipitation of secondary minerals.

The sorption to mineral surfaces will be controlled by competition for ion exchange sites by the various cations in solution. Initially, ion exchange sites in the alluvium are expected to be mainly filled with calcium. The sodium-bearing waste has a very high initial concentration (1.5 M) of sodium, and, upon contact with this solution, the sodium will replace most of the calcium on the exchange sites. The high sodium concentration will also compete with other cations, such as strontium (Sr-90) and cesium (Cs-134 and Cs-137), for exchange sites. Both strontium and cesium are cations characterized by low ionic potential (valence/ionic radius) and weak hydration. As a result, the primary mode of interaction of Cs and Sr with mineral surfaces is ion exchange (Appelo and Postma 1996). In ion exchange, the cation forms an outer sphere complex with a mineral surface to balance fixed charge deficit caused by ionic substitution within the mineral lattice. Clays are the predominant source of cation exchange capacity in most sediments, although manganese minerals can also provide some cation exchange capacity. Strontium exchanges with planar sites on clays. Cesium, however, can exchange both with planar sites and with frayed-edge sites on clays (Zachara et al. 2002). The binding to the frayed-edge sites is much stronger than to the planar ion exchange sites. As a result, Cs shows a very strong binding to clays at low concentrations, with weaker binding at higher concentrations. At least two ion exchange sites (and sometimes more) are commonly used to model the sorption of cesium to clay minerals (Zachara et al. 2002; Steefel et al. 2003). Ion exchange reactions are relatively rapid, and an equilibrium model can be used for Sr and Cs sorption in tank farm backfill.

### 1.3 Geochemical Model Overview

For relatively large alkali-earth cations with low hydrated ionic charge density, such as strontium, sorption to soil surfaces will mainly occur through formation of outer-sphere complexes at fixed-charge sites on the planar surfaces of clay minerals. The formation of these outer-sphere complexes is described by cation exchange theory. A general expression for the cation exchange reaction is (Appelo and Postma 1996)



where

$S_i$  and  $S_j$  = cations i and j with charges  $z_i$  and  $z_j$

$X$  = cation exchange site.

For example, the exchange of strontium for sodium on cation exchange sites is given by



Because strontium has a charge of +2, it displaces two sodium ions and occupies two ion exchange sites. The activity of the cations on the ion exchange sites follows the Gains-Thomas convention and is given by the equivalent fraction. The equilibrium equation based on the law of mass action is

$$K_{Sr/Na} = \frac{a_{Na}^2 \left[ \frac{2 \cdot m_{SrX_2}}{X_T} \right]}{a_{Sr} \left[ \frac{m_{NaX}}{X_T} \right]^2} \quad (3)$$

where

- $K_{Sr/Na}$  = selectivity coefficient for Sr – Na exchange
- $m$  = molality of surface exchange species (mole/L)
- $X_T$  = cation exchange capacity (mole/L)
- $a$  = free ion activity of the cation.

When strontium is present in low concentrations relative to sodium, it is sometimes assumed that the aqueous and sorbed concentrations of sodium do not change significantly during the sorption process, allowing Equation (3) to be simplified to

$$K_{Sr/Na} \frac{\left[ \frac{m_{NaX}}{X_T} \right]^2}{a_{Na}^2} \cdot \frac{X_T}{2} \frac{\rho}{\theta} = \frac{C_{Sr-sol}}{C_{Sr-dis}} = K_d \quad (4)$$

where

- $\gamma$  = activity coefficient for strontium in solution
- $\rho$  = bulk density of solid (kg/L)
- $\theta$  = water content (L/L)
- $C_{Sr-sol}$  = concentration sorbed to solid (mole/kg)
- $C_{Sr-dis}$  = concentration dissolved in solution (mole/L).

All the terms moved to the left side of Equation (4) indicate the wide range of parameters that are implicitly assumed constant to apply a  $K_d$  approach to reactive transport.

For the leak of sodium-bearing waste at CPP-31, the aqueous concentration of sodium changes several orders of magnitude so that both the aqueous concentration and the equivalent fraction of sodium on the ion exchange sites undergo significant changes. In conjunction, parallel reactions are taking place, particularly with calcium being released by dissolution of calcite, and the resultant competition for the same ion exchange sites. Using the cation exchange modules in TOUGHREACT (Xu et al. 2004), we can explicitly include competitive cation exchange reactions in the transport simulation in addition to

including the precipitation/dissolution processes. In adopting this mechanistic approach to simulating the evolution of the released sodium-bearing waste, the first-order equilibrium  $K_d$  is explicitly not considered.

## **2. DATA NEEDS**

To implement competitive cation exchange in TOUGHREACT, the following information must be known or estimated:

- Cation exchange capacity
- Selectivity coefficients for all significant cations
- Pore water and infiltration water chemistry
- Composition of cations occupying the exchange sites on the sediment.

This list is not independent. Given the pore water composition and the selectivity coefficients, the composition of the exchange assemblage will be fixed. Therefore, only two of the last three items need to be known to complete the model. The following sections review existing data to determine if representative value or values for each parameter can be determined.

### **2.1 Cation Exchange Capacity**

Because of internal lattice substitutions in clay minerals, the minerals have a net negative surface charge that is independent of pH. Additional negative surface charge may develop along the edges of the clay plates as pH rises, but this is usually not a significant fraction of total surface charge for illite and smectite clays (McBride 1994), which are the predominant clays in INL Site alluvial sediments (Bartholomay et al. 1989). Cations are sorbed to the clay mineral surface by electrostatic attraction based on this charge. The total negative charge present to bind cations is termed the cation exchange capacity (CEC).

#### **2.1.1 Analytical Method Comparability**

To measure CEC, a soil sample is placed in contact with a solution containing a high concentration of one cation, usually sodium or ammonium. This contacting solution is replaced several times until all of the exchange sites on the soil are occupied by a single type of cation. Then, the soil is placed in contact with a solution containing a different cation, such as potassium, which exchanges for the first cation. The amount of the first cation in the solution following exchange gives the CEC of the sediment.

The most common method analysis during the 1950s used ammonium-acetate buffered at pH 7 for the initial solution to saturate the exchange sites (McBride 1994). For calcareous soils, such as the Big Lost River gravels, this may result in dissolution of calcite. Calcium released by dissolution will compete with the ammonium for exchange sites on the clays during the saturation step. As a result, the Method can be biased low for total CEC. An improved method is to buffer the solution at pH 8.2, as is included in EPA Method SW 9081 (EPA 1986). Dissolution of soil carbonate minerals will be minimized, decreasing the potential for calcium to prevent complete saturation of exchange sites by sodium.

#### **2.1.2 Existing Data Sources**

Review of the INL literature and the Environmental Data Warehouse showed three primary periods of sampling for analysis of CEC on Big Lost River sediments in the vicinity of INTEC. The first round of sampling was conducted during the initial assessment of the National Reactor Testing Station (now

the Idaho National Laboratory Site) in the mid 1950s by the U.S. Geological Survey (USGS). The second round was conducted in the mid 1960s, and the third round was conducted in the early 2000s for ecological risk assessment. Excavation of the alluvium during construction of the tank farm would have mixed the material and destroyed any layering from original deposition. Photographs taken during construction of the tanks show evidence that materials were not sorted or size-segregated before being backfilled into the excavation. During construction projects, additional material has been added to the tank farm from nearby gravel pits when backfill was needed. Therefore, alluvial material in the tank farm will have the same average geochemical properties as Big Lost River alluvium outside the tank farm. Because of the mixing, sediments with higher-than-average CEC or lower-than-average CEC will have been mixed with material with average CEC properties. Therefore, tank farm backfill may not show as wide a range of properties as undisturbed alluvium.

The USGS collected surface sediment samples as part of the initial INL site characterization (Nace et al. 1956). The method used to determine the CEC is not explicitly stated. Lacking specific information, the assumption is that the method used ammonia-acetate buffered at pH 7. The CEC results may be biased low because of calcium released by dissolution of calcite, but there is insufficient information to be certain. There is an extensive discussion of the distribution of CEC with grain size, and the authors state:

“it is believed that the exchange values reported .... are in the correct order of magnitude for the total exchange capacity of the gross parent samples.”

Based on this, the conclusion is that the mass of large particles separated before determination of the CEC was then added back to correct the CEC measurements to total bulk sample mass.

The data have been divided into INTEC-specific CEC measurements and CEC measurements from the general central INL Site area (Table 1). The box around INTEC in Figure 1 shows the locations that are considered INTEC-specific. Locations at the southern end of the map are near the Central Facilities Area landfills. All of the locations on the map are in alluvial gravel of the Big Lost River based on geologic maps of the area. The Big Lost River has been fed from the same source area during the entire period that the alluvium was being deposited and shows similar mineralogy (Bartholomay et al. 1989). Given similar source area, mineralogy, grain-size distribution, and depositional environment for the area depicted in Figure 1, sediment samples throughout this region would be representative of gravels at INTEC and within the tank farm.

Data from the USGS characterization studies are compiled in Table 14 of Bartholomay et al. (1989). Cross-referencing data in Table 14 with the map in Bartholomay's Figure 13 (reproduced here as Figure 1), 21 CEC measurements for Big Lost River alluvium from the INTEC vicinity can be identified. Nine of the samples are from the INTEC facility and an additional 12 samples from the general area near INTEC. Samples of alluvium for CEC measurements come from a range of depths from 1 to 44 ft (Table 1). CEC data at INTEC range from 1.8 meq/100 g to 4.5 meq/100 g. Outside the INTEC “box”, the CEC ranges from 2.1 meq/100 g to 3.9 meq/100 g. The means are 2.9 meq/100 g for INTEC and 3.2 meq/100 g for the area and are not significantly different at the 90% confidence level. Because the data at INTEC and the data in the central INL Site area overlap and the means are not significantly different, the data are grouped and overall statistics are calculated for the samples. The mean is 3.05 meq/100 g with a 95% confidence range from 2.71 to 3.40 meq/100 g. Twenty-one samples from a rather large area of the central portion of the INL Site, all representing alluvium of the Big Lost River, show little variation in CEC. The total range is from about 2 to 4.5 meq/100 g with a mean of 3.0 meq/100 g. The USGS data are generally representative of Big Lost River alluvium in situ, with a possibility of a slight low bias depending on the method of measurement used.

Table 1. CEC measurements from alluvium in the central portion of the INL Site shown in Figure 1.

CEC (meq/100 g)	Map Location	Sample Level Top (ft)	Sample Level Bottom (ft)	INTEC or Area
1.8	83	8	8	INTEC
2.2	87	12	12	INTEC
3.4	88	NR	NR	INTEC
2.7	89	43	44	INTEC
2.9	90	6	7	INTEC
2.0	91	10	10	INTEC
4.5	91	12	12	INTEC
2.0	112	NR	NR	INTEC
4.5	112	NR	NR	INTEC
3.1	80	5	5.5	Area
2.9	80	10	10.5	Area
3.6	81	3	3.5	Area
3.4	82	12	12	Area
2.3	82	14	14	Area
2.5	84	5	5	Area
3.7	85	5	5	Area
3.9	86	5	5	Area
3.7	92	4	5	Area
3.2	93	1	2	Area
2.1	94	5	5	Area
3.7	113	NR	NR	Area

NR = not reported.



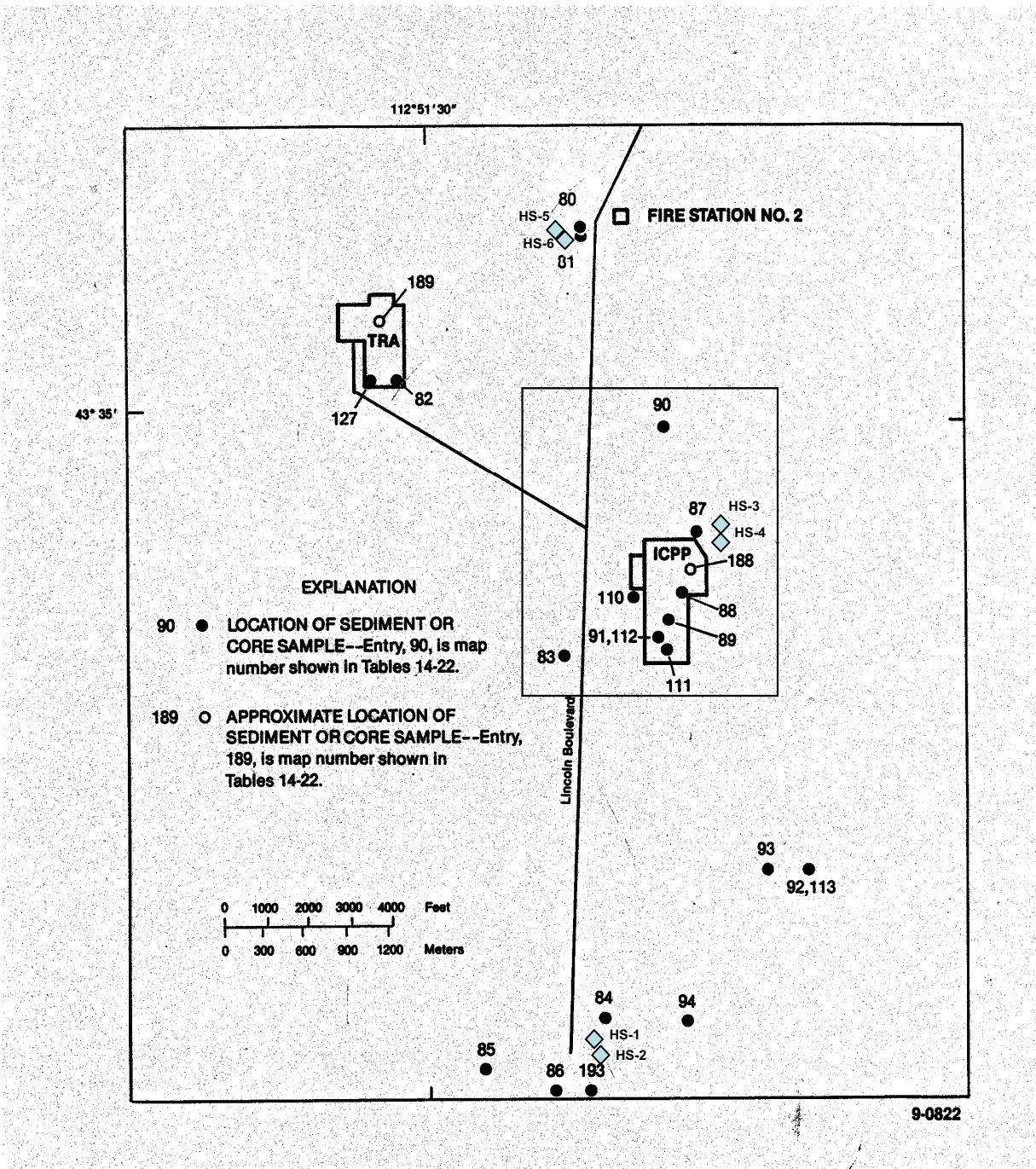


Figure 1. Map of the central portion of the INL Site showing the locations of samples from which CEC data are available. Black numbered circles are data from Nace et al. (1956) and measured CEC values are shown in Table 1. Blue triangles are approximate locations where samples were collected for Hawkins and Short (1965) strontium sorption study. Map from Bartholomay et al. (1989).

An early investigation into the sorption of Sr and Cs by sediments at the INL Site was conducted by Hawkins and Short (1965). They measured CEC on composite samples made up from alluvial sediments collected in the vicinity of INTEC (Figure 1). Three different methods were used to measure CEC, and all methods gave good agreement. Solutions were not buffered, so calcite dissolution would have been minimized. Multiple measurements of CEC on the same material using the same method gave quite variable results ranging from 3.2 to 7.8 meq/100 g. CEC for Sr ranged from 7.9 to 12 meq/100 g, and for Cs ranged from 4.3 to 8.3 meq/100 g. Different exchange capacities for different ions are not uncommon (Zachara et al. 2002); however, the TOUGHREACT code can only handle a single CEC. Hawkins and Short (1965) sieved the alluvium to remove material larger than 2 mm. Sieve analyses of the Big Lost River alluvium from which the samples used by Hawkins and Short were taken are reported by Hawkins and Foster (Hawkins and Foster 1963). The sieve analyses indicate that 75% to 77% of the alluvium in the samples was greater than 2 mm. The Sr CEC for the Hawkins and Short samples can be adjusted by a factor of 0.24 to include the weight of the total alluvium assuming the > 2-mm fraction has zero CEC. The adjusted CEC values are on the order of 2 to 3 meq/100 g. Based on the agreement among different methods of CEC measurement and the ability to correct the CEC results to bulk alluvium using measured grain size analyses, the Hawkins and Short data are considered comparable to the earlier USGS results.

The sampling locations where the alluvium samples were collected are shown in Hawkins and Foster (1963) and are shown in Figure 1. The samples come from gravel pits just north of the Central Facilities Area, just east of INTEC and near Fire Station No. 2. These samples are from Big Lost River alluvium in similar depositional environments as the alluvium at INTEC and are therefore considered representative. Two samples collected northwest of the Reactor Technology Complex may not be from Big Lost River alluvium and were not included here.

During recent remedial investigations, 27 samples of surficial alluvium were collected just outside the INTEC fence to the north, east, south and west of the facility. The samples were composites and were collected either at the ground surface or between depths of 0 to 24 in. below the surface. In the field during sample collection, samples were screened through a No. 9 wire mesh with a reported particle size discrimination of 3.7 mm<sup>a</sup>. Grain-size distribution was not measured on these samples, so the fraction of sample weight removed cannot be calculated. CEC was determined by EPA Method SW 9081 (EPA 1986). In this method, exchange sites are saturated with sodium in a solution buffered at pH 8.2. By buffering the solution at pH 8.2, dissolution of soil carbonate minerals will be minimized, decreasing the potential for calcium to prevent complete saturation of exchange sites by sodium. The sodium is subsequently displaced by ammonium acetate solution, and the CEC calculated from the amount of displaced sodium. CEC measurements from these samples range from 4.3 to 20.3 meq/100 g with a median of 15.9 meq/100 g.

These numbers are significantly higher than earlier USGS measurements. Because of the particle size discrimination during sampling, these results are not representative of Big Lost River alluvium. The measured values cannot be corrected because grain-size information on the samples is lacking. The screen used does not match the size of sieves used for particle size analysis, and so a direct comparison between the screen size and other data on grain size analyses cannot be made. A statistical summary of grain-size properties of Big Lost River alluvium (Bartholomay et al. 1989) indicates a wide range in the percent of material greater than 2 mm. For Big Lost River channel deposits (Bartholomay et al. 1989, Table 7) the screening could have removed from as little as 15% of the sample material to as much as 80% of the sample material. In Bartholomay et al. (1989), Table 3, grain-size data from samples collected closest to

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a. This is not a 9-mesh Tyler screen, but a commercial wire screen. Personal communication, August 31, 2005, T. J. Haney, CH2M-WG Idaho, LLC, Idaho Cleanup Project.

INTEC are more uniform and suggest an average weight percent greater than 2 mm of about 60% (Bartholomay et al. 1989). Based on an assumption that 60% of the alluvial material would have been removed by screening, the 2000–2004 data were adjusted with a factor of 0.4 to estimate in situ Big Lost River alluvium CEC (Figure 2). The analytical method used to measure CEC should give comparable and representative data; the sample locations from INTEC provide representative material. Because of sample handling before analysis, however, the analytical data are neither representative nor comparable. An approximate correction can be made for this handling; however, the uncertainty in the final data is something like  $\pm 20\%$  based on the uncertainty in the size fraction analyzed.

Based on all available data, alluvial CEC in the tank farm will be low, on the order of a few meq/100 g. Data from the USGS collected in 1956 and from Hawkins and Short (1965) are representative of the CEC of bulk alluvium. Data from the two studies are in agreement even though the method of CEC measurement is different. Data collected for an ecological risk assessment are not representative of bulk alluvium properties.<sup>b</sup> A correction can be made to adjust for removal of gravel, but uncertainty remains  $\pm 20\%$  for these measurements. CEC measurements range from about 2 to about 8 meq/100 g (Figure 2), with the most reliable data falling between 2 and 5 meq/100 g. Given the consistency of CEC measurements from across a number of locations and sampling depths in the alluvium along the Big Lost River and agreement between the 1956 USGS data and the 1965 Hawkins and Short data, we conclude that the CEC of the alluvium at INTEC will fall within a narrow range from about 2 to 5 meq/100 g with an average near 3 meq/100 g.

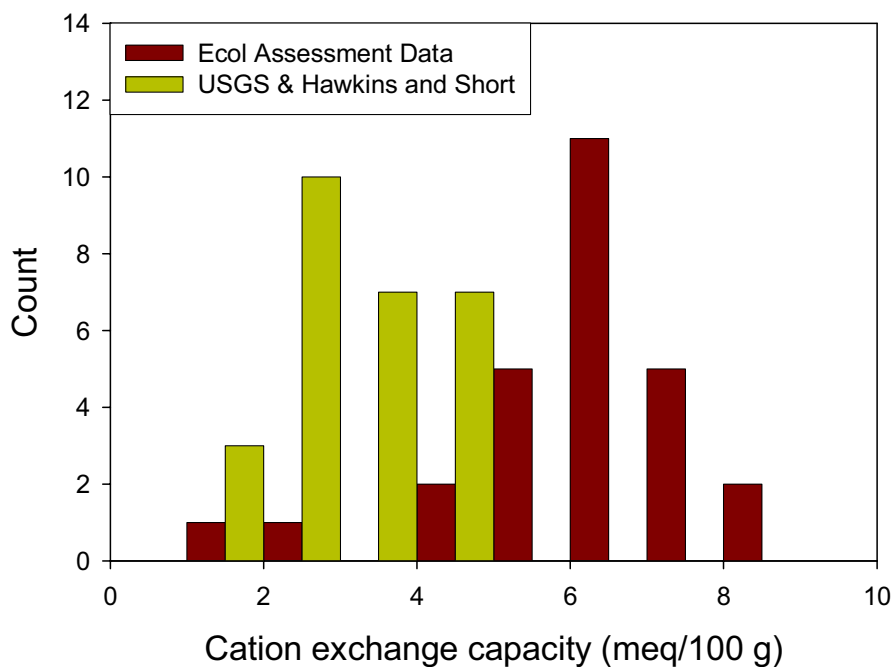
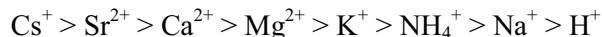


Figure 2. Histogram of measured cation exchange capacity for Big Lost River alluvium near INTEC. Data for the 2000+ sampling period were adjusted by a factor of 0.4 to account for the estimated grain-size discrimination during sample collection. USGS data are from 1956 and are not adjusted. Hawkins and Short (1965) CEC measurements are adjusted based on measured grain-size analyses.

b. Personal communication, August 31, 2005, T. J. Haney, CH2M-WG Idaho, LLC, Idaho Cleanup Project.

## 2.2 Selectivity Coefficients

There is a distinct preference for certain cations on ion exchange sites, with preference given to those cations with larger *hydrated* ionic potentials (Appelo and Postma 1996). This order of preference is given in lyotropic series presented by a number of authors:



The order of preference in these series show widespread agreement (McBride 1994; Appelo and Postma 1996; Sparks 2003), indicating that selectivity coefficients show a consistent order of preference across a range of sediment materials. The consistent order of selectivity indicates that cation properties are more important for determining ion selectivity than are material properties. We conclude from this that ion exchange selectivity coefficients taken from the literature will provide a good starting point for the ion exchange model. In the results presented here, ion exchange selectivity coefficients were taken from Appelo and Postma (1996), Table 5.5, p. 160, because this table provides a fairly comprehensive set of exchange coefficients that are comparable and includes all the components of primary interest for the tank farm. These coefficients are given for the Gaines-Thomas convention and written in terms of one sodium ion reacting. The coefficients are, therefore, in the same form as used in TOUGHREACT. Ion exchange selectivity coefficients adopted for the model are shown in Table 2. Hydrogen ion was adopted from Appelo (1994). Because the hydrogen ion is so tightly hydrated, it has a very low hydrated ionic potential and does not compete readily for ion exchange sites (McBride 1994). Because of the low pH of the sodium-bearing waste, however, there may be appreciable concentrations of hydrogen ion, so it is included in the model.

Table 2. Ion exchange selectivity coefficients from Appelo and Postma (1996) or Appelo (1994) used in the validation of the ion exchange model.

Ion +1	$K_{\text{Na}/i}$	Ion +2	$K_{\text{Na}/i}$
H	7.7E+5	Mg	0.50
Na	1.00	Ca	0.40
NH <sub>4</sub>	0.25	Sr	0.35
K	0.20		
Cs	0.08		

No measurements of site-specific ion exchange selectivity coefficients have been made for Big Lost River alluvium. There have been many measurements of partition coefficients for Sr ( $K_d$  values). Some of these even included testing the effects of competing cations on the  $K_d$  value (Hawkins and Short 1965; Bunde et al. 1997; Liszewski et al. 1997; Bunde et al. 1998; Liszewski et al. 1998). Only Hawkins and Short (1965) report the CEC value associated with the sediments used in the experiments. Therefore, the Hawkins and Short data can be used to evaluate applicability of these exchange coefficients (Table 2) to Big Lost River alluvium. This evaluation will be reported in Section 6.2.

## 2.3 Pore Water Chemistry and Solid Phases

Parameterization of the remainder of the geochemical model includes the incorporation of sodium-bearing waste chemistry, pore water and recharge water chemistry, and solid phase geochemical properties.

### 2.3.1 Sodium-Bearing Waste Composition

The composition of the sodium-bearing waste is taken from Rhodes (1972) for Tank WM-181. The components of sodium-bearing waste important for strontium transport are given in Table 3. Hydrogen ion is important because it will dissolve calcite and release calcium. Hydrogen and sodium are possible competitors with strontium and cesium for exchange sites. Nitrate provides charge balance but can also form soluble complexes with strontium at high nitrate concentrations, which increases strontium mobility. Aluminum will primarily play a role in buffering the pH at low values through precipitation of aluminum hydroxide minerals.

Table 3. Components of sodium-bearing waste included in reactive transport model. Other components were present at concentrations much less than these and were not considered in the model.

Component	Concentration (Reported) <sup>a</sup>	Units	Concentration (mole/L) <sup>b</sup>	Activity (Ci/L)
H <sup>+</sup>	1.4	M	1.5	NA
NO <sub>3</sub> <sup>-</sup>	4.38	M	4.5	NA
Na <sup>+</sup>	36.6	g/L	1.5	NA
Al <sup>+++</sup>	0.56	M	0.5	NA
Cs-134	3.74E+04	dps/mL	5.834E-09	1.01E-03
Cs-137	8.81E+06	dps/mL	2.016E-05	2.38E-01
Cs (tot)			2.019E-05	NA
Sr-90	7.91E+06	dps/mL	1.74E-05	2.14E-1

a. Rhodes (1972), sodium-bearing waste chemical analysis WM-181.

b. Used in model.

NA = not applicable.

### 2.3.2 Pore Water and Recharge

The geochemistry of perched water at INTEC has been reported in Roddy (2005). The chemistry of the perched water is highly variable (Table 4) because multiple sources of recharge contribute to the perched water. In spite of the range in chemical composition, the perched zone waters are close to saturation with respect to calcite in equilibrium with a soil gas phase at a partial pressure of carbon dioxide of around 10<sup>-2</sup> atm. These two geochemical constraints were placed on the composition of the pore water. We then took the minimum sodium and chloride concentrations in perched water (0.3 mmol/L) for background electrolyte. This set of parameters allows all the significant components of the sodium-bearing waste and all the significant chemical reactions in the geochemical model to be incorporated into the model. One final condition was set on the pore water with the aluminum concentration set by equilibrating the water with gibbsite. Minimizing the number of components in the system, we set the initial pore water and recharge to be a low-molality sodium-chloride solution saturated with respect to calcite at a partial pressure of CO<sub>2</sub>(g) of 10<sup>-2</sup> atm. This reflects an increase in carbon dioxide over atmospheric from microbial activity in the subsurface. The resulting chemical composition alluvium pore water is shown in Table 5. The same water composition was used for the pore water at the start of the simulation, as well as the composition of the recharge water. Note that this pore water contains stable natural strontium. One of the sensitivity analysis presented here evaluates the effect of including or excluding the natural strontium from the geochemical model on the transport of radioactive Sr-90.

Table 4. Summary statistics for perched water in the vadose zone at the north end of INTEC (Roddy 2005).

Parameter	Unit	Maximum	Minimum	Mean	No. of Samples
Ca	mmol/l	2.92	0.75	1.61	62
Na	mmol/l	4.65	0.32	1.72	62
K	mmol/l	0.54	0.05	0.15	62
Mg	mmol/l	1.77	0.07	0.74	62
Sr	mmol/l	0.007	0.003	0.004	15
Cl	mmol/l	5.78	0.33	1.41	67
SO <sub>4</sub>	mmol/l	0.69	0.02	0.32	67
HCO <sub>3</sub>	mmol/l	8.87	0.39	3.53	65
Temp	°C	20.50	9.60	15.36	16
pH		8.10	7.02	7.51	20
log P <sub>CO2</sub>	atm	-1.67	-2.95	-2.26	21
Saturation index for calcite		0.51	-0.31	0.03	21
Saturation index for strontianite		-1.41	-1.88	-1.70	7

Table 5. Pore water and recharge water composition. This water is a low-ionic-strength sodium-chloride solution saturated with respect to calcite at a partial pressure of carbon dioxide of 0.01 atm.

Component	Concentration (mmol/L)
H <sup>+</sup>	5.369E-05
pH	7.30
Ca <sup>+2</sup>	1.64
Sr <sup>2+</sup>	0.007
Na <sup>+</sup>	0.33
Cl <sup>-</sup>	0.33
HCO <sub>3</sub> <sup>-</sup>	3.64

### 2.3.3 Solid Phase Geochemical Properties and Parameters

The tank farm was constructed by excavating the alluvium at INTEC to bedrock, building the tanks, and then backfilling around the tanks. The alluvium at INTEC contains both Big Lost River channel deposits, and Big Lost River overbank deposits, which, during construction, would have been well homogenized. The backfill material is assumed to be homogeneous and representative of typical Big Lost River alluvium. Big Lost River alluvium in the vicinity of INTEC has been characterized for selected geochemical characteristics (Hawkins and Short 1965; Bartholomay et al. 1989; Del Debbio and Thomas 1989; Liszewski et al. 1997, 1998; Rosentreter et al. 1999). Table 6 summarizes the mineralogic composition.

Clay minerals identified in the field samples are dominantly illite, smectite, and mixed-layer illite/smectite with smaller amounts of kaolinite (Bartholomay et al. 1989). Calcite is common. Dolomite is less common and would be much slower to react with acid. Dolomite is left out of the model so that Mg can be left out of the model for simplification. Considering the mixing that took place, a range of calcite contents of 3 to 7 wt% would be expected in the alluvium, with a value of 5 wt% identified as the midpoint. Del Debbio and Thomas (1989) characterized INTEC alluvium as part of a  $K_d$  investigation, and determined calcite to be 5.6 wt%, which is in agreement with the USGS data. For a site-wide investigation of strontium adsorption to surficial sediment, Liszewski et al. (1997) measured mineralogy of INTEC alluvium for three samples (Table 6). The mineralogy of these samples, including calcite, correspond to other measurements of mineralogy in INTEC alluvium. Table 7 gives mineral parameters needed to convert among weight percent, moles, and volume percent. The specific gravity of alluvium grains is very consistent at  $2.725 \pm 0.022$  (2 std dev) g/cm<sup>3</sup>. Five wt% calcite in the alluvium solids converts to 5.03 vol% of calcite in the alluvium solids (cm<sup>3</sup> calcite/cm<sup>3</sup> alluvium). Other values adopted for the alluvium are bulk density of 1.8 g/cm and porosity of 0.33 cm<sup>3</sup>/cm<sup>3</sup>.

Mass balance calculations indicate that sufficient calcite is present in the alluvium to react with (i.e., neutralize) the acid in the sodium-bearing waste. However, depending on the distribution of flow, significant acidity could remain if flow was concentrated along a few flow paths. If significant acidity remains unbuffered after calcite is consumed, then other minerals can be included in the model to dissolve more slowly by a kinetic reaction and provide additional pH buffer capacity.

Table 6. Mineralogy of Big Lost River channel and overbank deposits. Values are weight percent.

Mineral	Channel Deposits <sup>a</sup> (n = 11)		Overbank Deposits <sup>a</sup> (n = 5)		INTEC Alluvium <sup>b</sup> (n = 3)
	Range	Median	Range	Median	Range
Quartz	32–45	38	27–37	33	41–56
Plagioclase	16–30	23	11–19	16	18–21
K-feldspar	6–18	12	9–15	12	0–13
Calcite	0–6	3	3–12	7	3–12
Pyroxene	8–14	12	5–10	8	0–14
Dolomite	0–3	0	3–7	6	0–0
Clays	8–14	10	14–27	19	0–22

a. Bartholomay et al. (1989).

b. Liszewski et al. (1997).

Table 7. Mineral properties for converting between mass and volume.

Mineral	Molar Volume (cm <sup>3</sup> /mole)	Molecular Weight (g/mole)	Mineral Density (g/cm <sup>3</sup> )
Calcite	36.934	100.087	2.710
Gibbsite	31.956	78.004	2.441

## 2.4 Equilibrium Exchange Assemblage

The ratio of cations on ion exchange sites on a clay is related to the ratio of cations in solution by the selectivity coefficients. Once the selectivity coefficients and pore water chemistry are defined, the initial exchange assemblage on the clays is fixed. Using the pore water chemistry defined in Table 5 and the selectivity coefficients defined in Table 2, the surface exchange assemblage can be calculated and is shown in Table 8.

No measurements of equilibrium exchangeable cations have been made on sediments from INTEC. Measurements have been made on sediments from the Subsurface Disposal Area (SDA) (Table 9). Divalent cations, calcium plus magnesium, make up about 95% of the exchangeable cations, with monovalent cations consisting of about 5%. This is in general agreement with the values calculated here, so the equilibrium exchange assemblage shown in Table 8 is adopted for the model of the alluvium.

Table 8. Surface exchange assemblage for clay minerals calculated in equilibrium with pore water.

Exchange Species	Concentration (mole/L)	Equivalent Fraction
CaX <sub>2</sub>	0.196	0.994
SrX <sub>2</sub>	0.00063	0.003
NaX	0.0012	0.003
Total	0.198	1.000

Table 9. Hawkins and Short (1965) solution chemistry and calculated composition of the cation exchange sites using the Appelo and Postma (1996) selectivity coefficients. Measured equivalent fractions from the SDA are shown for comparison.

Component	Dissolved (mg/L)	Dissolved (mmol/L)	Sorbed (mmol/L)	Equivalent Fraction (model)	Equivalent Fraction (measured SDA)
Na	163	7.09	0.156	0.049	0.02
K	25	0.64	0.070	0.022	0.03
NH <sub>4</sub>	25	1.39	0.116	0.036	Not available
Ca	125	3.12	1.100	0.696	0.75
Mg	31	1.28	0.311	0.196	0.20



### **3. VERIFICATION OF THE ION EXCHANGE MODEL**

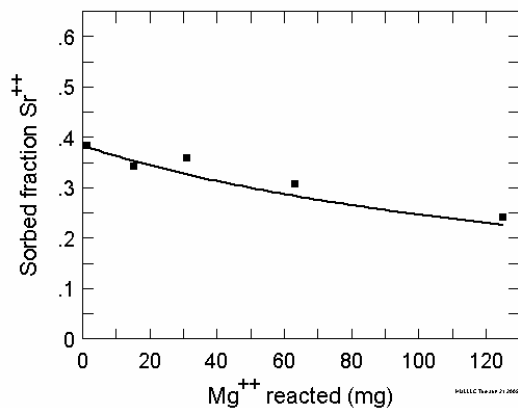
Because ion exchange depends on the ionic potential of the hydrated ion, much of the ionic selectivity is due to the aqueous ion and not the surface. Therefore, as an initial starting point, selectivity coefficients from the literature are appropriate. However, verification of the ion exchange parameters would enhance the level of confidence in the geochemical model. The investigation conducted by Hawkins and Short (1965) provides a dataset that can be used to verify the model. These authors measured the effect of competing ions, including calcium, magnesium, sodium, potassium, ammonium, and hydrogen, on the sorption of Sr and Cs to INTEC alluvial sediments. Strontium and cesium adsorption data were digitized from graphs presented in Hawkins and Short, and experimental solution chemistry was taken from water compositions given in the report. The cation exchange capacity of the sediment used in these calculations was 8 meq/100 g, which is intermediate between their high and low exchange capacity sediments. Their experiments consisted of 25 mL solutions contacted with 1 g of sediment. Scaling this to 1 L of solution gives 1,000/25 or 40 g/L and results in 40 g of sediment and 8 meq/100 g of CEC in a single liter of test solution. This gives 3.2 mM of exchange sites per experiment.

To perform the verification calculations, the exchanging mineral surface was first equilibrated with the test solution containing all cations at the primary concentration. This equilibration gives a total moles of each cation in the system, which is summed over the dissolved species and the cation exchange sites. The equivalent fraction (modeled) column in Table 9 shows the equivalent fraction for each ion on the soil surface calculated using the Appelo and Postma (1996) selectivity coefficients. Measured equivalent fractions for SDA interbed sediments (Leecaster and Hull 2003) are shown in the final column. While these materials are interbeds from a different facility, the relative magnitude of the calculated values are close to the measured values. Calcium dominates the CEC sites, with the other predominant divalent cation, Mg, filling the second largest number of sites.

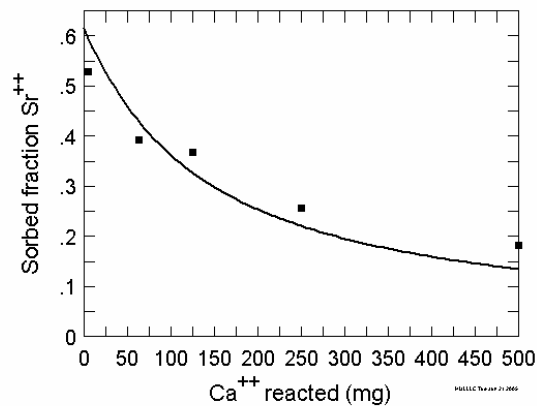
In the Hawkins and Short (1965) Sr experiments, radioactive Sr-85 was added to the solutions at a concentration of 50  $\mu\text{Ci/L}$ . Converting 50  $\mu\text{Ci/L}$  of Sr-85 gives  $2.48\text{E-}11$  mole/L of Sr. This is the value of Sr used in modeling the adsorption experiments. Cs adsorption experiments were run at 5 mg/L total Cs. Radioactive Cs was used as a tracer.

#### **3.1 Comparison of the Ion Exchange Model to the Hawkins and Short Strontium Experiments**

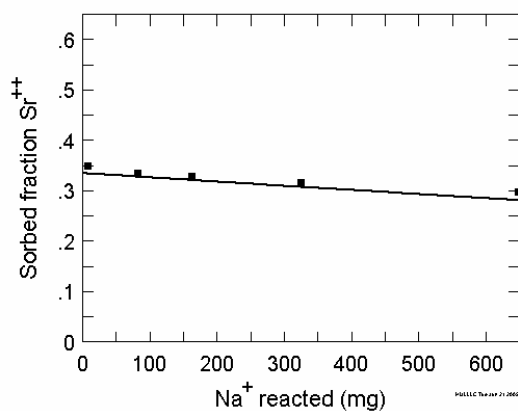
The Hawkins and Short (1965) strontium ion exchange experiments were simulated using the Appelo and Postma (1996) selectivity coefficients. Hydrogen ion was added using a selectivity coefficient from Appelo (Appelo 1994). All of the Hawkins and Short Sr adsorption experiments (Figure 3 A to D) were matched very well with no modifications to the CEC or the selectivity coefficients. The hydrogen ion is very strongly hydrated and has a relatively small charge. As a result, it is not very competitive for exchange sites. There is very little effect of pH on Sr exchange (Figure 4).



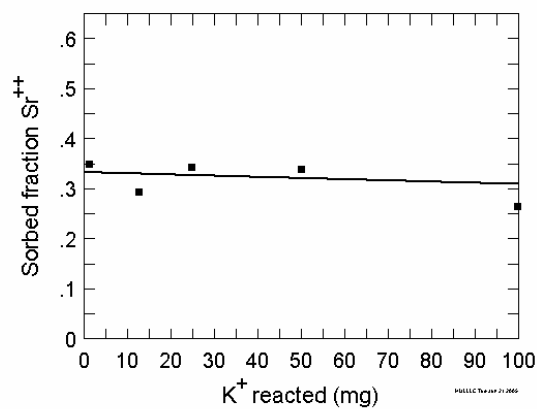
A



B



C



D

Figure 3. Plot of sorbed Sr fraction as a function of competing cation concentration in solution. The amount of metal reacted is the concentration of the competing cation (mg/L) in solution. Points are measured values from Hawkins and Short (1965). Line is a model using selectivity coefficients from Appelo and Postma (1996).

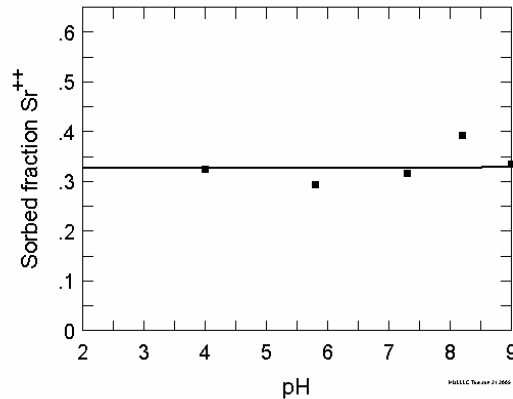


Figure 4. Plot of sorbed Sr fraction as a function of pH of solution. Points are measured values from Hawkins and Short. Line is a model using selectivity coefficients from Appelo and Postma (1996). For H<sup>+</sup>, the selectivity coefficient is 7.7E+05.

The selectivity coefficients take from Appelo and Postma do an excellent job of matching the sorption of strontium to INTEC sediments. The ion exchange model is given below:

Monovalent

>X:Na <sup>+</sup> + Na <sup>+</sup>	= >X:Na + Na <sup>+</sup>	Selectivity coef = 1.00
>X:NH <sub>4</sub> <sup>+</sup> + Na <sup>+</sup>	= >X:Na + NH <sub>4</sub> <sup>+</sup>	Selectivity coef = 0.25
>X:K <sup>+</sup> + Na <sup>+</sup>	= >X:Na + K <sup>+</sup>	Selectivity coef = 0.20
>X:H <sup>+</sup> + Na <sup>+</sup>	= >X:Na + H <sup>+</sup>	Selectivity coef = 7.7E+05

Divalent

0.5 >X <sub>2</sub> :Mg + Na <sup>+</sup>	= >X:Na + 0.5 Mg <sup>++</sup>	Selectivity coef = 0.50
0.5 >X <sub>2</sub> :Ca + Na <sup>+</sup>	= >X:Na + 0.5 Ca <sup>++</sup>	Selectivity coef = 0.40
0.5 >X <sub>2</sub> :Sr + Na <sup>+</sup>	= >X:Na + 0.5 Sr <sup>++</sup>	Selectivity coef = 0.35

### 3.2 Comparison of the Ion Exchange Model to the Hawkins and Short Cesium Experiments

Cesium ion exchange has frequently been found to be more complicated than strontium. Zachara et al. (2002) show that Cs is not only sorbed by ion exchange to planar sites on the surfaces of clay minerals but by ion exchange to frayed-edge sites. Ion exchange is considered to be the mechanism for both sites, because Zachara et al. found no evidence for pH effects on Cs adsorption to clays. Two ion exchange sites were needed to fit the Hawkins and Short (1965) data for Cs. For the planar sites, the selectivity coefficients for the ions other than Cs are the same as used for Sr. Cs exchange is much stronger than indicated by the Appelo and Postma (1996) selectivity coefficient (Table 2), and the CsX exchange coefficient was significantly increased (Table 10). The first plot matched was the plot of Cs sorption as a function of Cs concentration. To achieve the high sorbed fraction at low Cs concentrations, the strong exchange frayed-edge site was needed in the model. The frayed-edge site was estimated by fitting the data visually. The CEC for the frayed-edge site is 3.25E-03 meq/100 g. The properties for the site are

>F:Na + Na <sup>+</sup>	= >F:Na + Na <sup>+</sup>	Selectivity coef = 1.00
>F:K + Na <sup>+</sup>	= >F:Na + K <sup>+</sup>	Selectivity coef = 0.006
>F:Cs + Na <sup>+</sup>	= >F:Na + Cs <sup>+</sup>	Selectivity coef = 2E-07.

Table 10. Ion exchange selectivity coefficients from Appelo and Postma used in the validation of the ion exchange model.

Ion +1	$K_{Na/i}$	Ion +2	$K_{Na/i}$
H	7.7E+5	Ca	0.40
Na	1.00	Sr	0.35
K	0.20	Mg	0.50
Cs	0.0006		
NH <sub>4</sub>	0.25		

This gives a reasonable good match to the Hawkins and Short (1965) data (Figures 5 and 6), but the plot in Hawkins and Short is limited in terms of the range of conditions covered. The fit is shown in linear and logarithmic forms (Figure 5) to show that the values of selectivity coefficient selected for formation of this species do not seem to overly estimate adsorption at low Cs concentrations. Hawkins and Short experiments were mostly run at 5 mg/L total Cs concentration.

The selectivity coefficient for Cs in Appelo and Postma (1996) was not strong enough to match the data. More sorption of Cs to INTEC sediments was measured by Hawkins and Short (1965) than is calculated using the Appelo and Postma coefficient of 0.08. The selectivity coefficient was estimated by fitting the Hawkins and Short data by visual inspection. The low-capacity CEC data were used in the fitting exercise. The final selectivity coefficient for planar ion exchange sites adopted for INTEC sediment is 0.0063.

Elevated concentrations of K and NH<sub>4</sub> decrease the sorption of Cs to clays to a greater extent than the model predicts (Figure 7). This is the poorest fit obtained, and the model underestimates the selectivity for Cs and NH<sub>4</sub>. However, changing the NH<sub>4</sub> selectivity coefficient would also change the Sr plot, which showed a good match. Given the low likelihood of significant NH<sub>4</sub> concentrations in the tank farm sediments, this is not considered a problem.

Hawkins and Short did not measure the change in Cs partitioning with pH. However, Cs sorption is little affected by changes in pH (Zachara et al. 2002). The calculated change in sorbed fraction is very small over the pH range 0 to 9 (Figure 8). The increase in sorbed fraction at low pH can be attributed to changes in the ion activities in solution as ionic strength gets large near pH 0.

The TOUGHREACT code only has provision for one type of CEC site. Therefore, the two-site model cannot be directly implemented in the code. This only affects cesium sorption and not strontium sorption. The total cesium concentration from the sodium-bearing waste is on the order of 2E-05 molar (Table 3). The estimated number of frayed-edge sites in the alluvium ranges from 1.7E-04 to 5.8E-04 molar, depending on the moisture content of the alluvium. The frayed-edge sites are not anticipated to become saturated with cesium. The selectivity coefficient to the planar sites can be adjusted to mimic the adsorption of Cs to the frayed-edge sites. The partition coefficient is the product of the number of sites and the selectivity coefficient (Hull et al. 2004). Because the number of planar sites is much greater than the number of frayed-edge sites, the selectivity coefficient has to be decreased by the ratio of the number of planar sites to frayed-edge sites. This gives a final selectivity coefficient for Cs on planar sites of 0.0006 (Table 10).

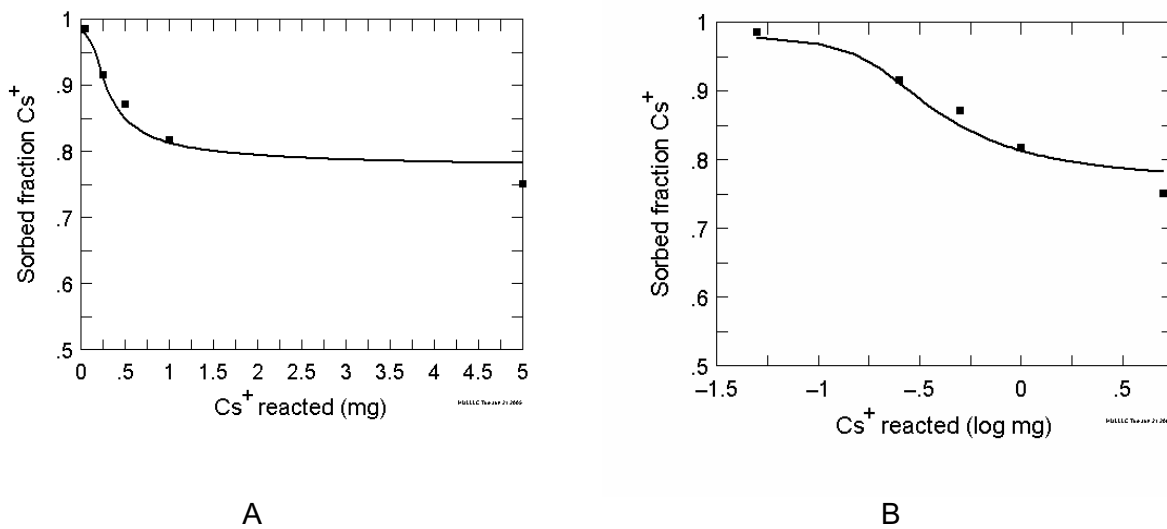


Figure 5. Plot of sorbed Cs fraction as a function of total Cs added to solution. There is relatively strong sorption of Cs at low concentrations, which decreases as Cs concentrations increase. This is modeled as a strong frayed-edge site present at low concentrations that is filled first, followed by ion exchange on a planar site. Planar site CEC = 3.2 mM. Frayed-edge site CEC = 1.3E-03 mM.

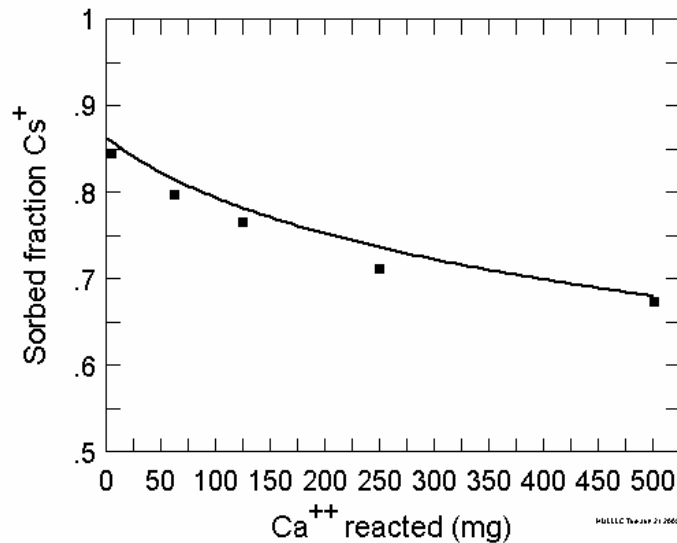
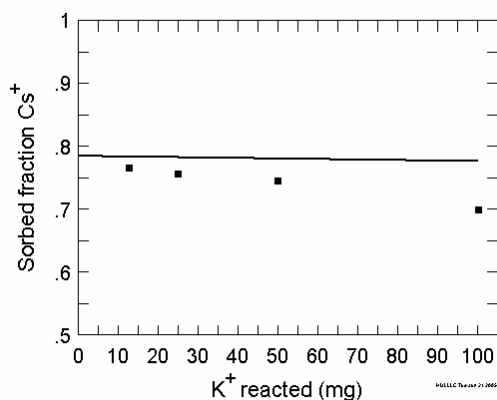
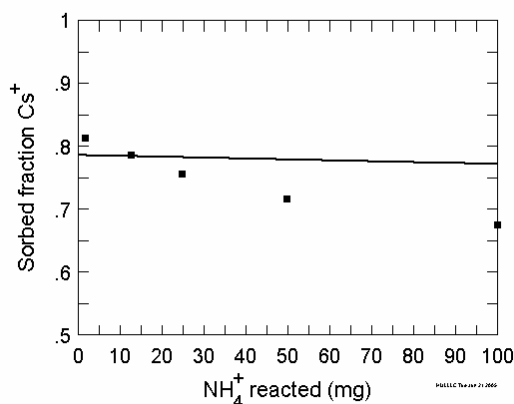


Figure 6. Plot of sorbed Cs fraction as a function of Ca ion concentration in solution. The amount of metal reacted is the concentration of the competing cation (mg/L) in solution. Points are measured values from Hawkins and Short. Line is a model using selectivity coefficients from Appelo and Postma except for Cs.

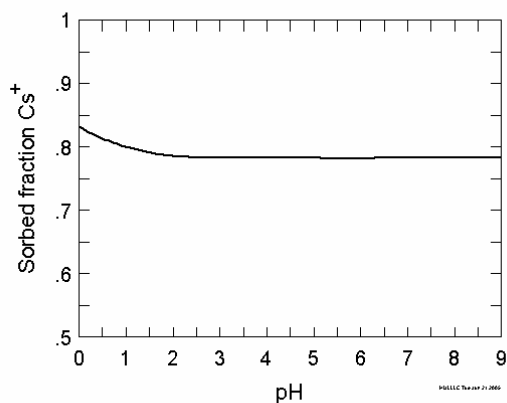


A

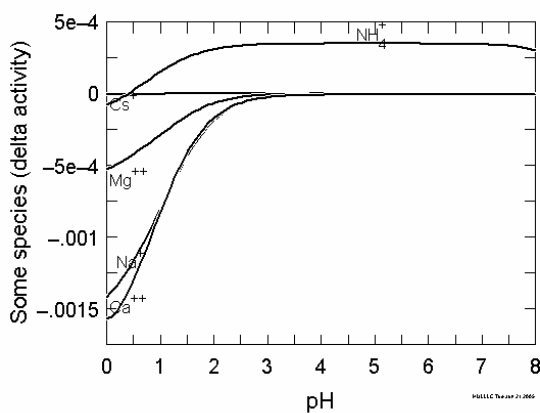


B

Figure 7. Plot of sorbed Cs fraction as a function of K and  $\text{NH}_4$  ion concentrations in solution. The amount of metal reacted is the concentration of the competing cation (mg/L) in solution. Points are measured values from Hawkins and Short. Line is a model using selectivity coefficients from Appelo and Postma except for Cs.



A



B

Figure 8. Panel A is a plot of sorbed Cs fraction as a function of pH in solution. Hawkins and Short did not measure the effect of pH on Cs sorption. Line is a model using selectivity coefficients from Appelo and Postma except for Cs. Panel B shows the change in ion activity due to the increase in ionic strength as pH approaches 0. Cs, being a small monovalent ion, changes much less than the divalent cation, resulting in a change in solution activity ratios even though the concentration ratios do not change.

Selectivity coefficients for cation exchange are primarily dependent on ionic properties rather than sediment properties. The general agreement in the relative order of cation selectivity among numerous authors indicates general wide agreement on the relative magnitudes of selectivity coefficients. Hawkins and Short conducted experiments on competitive adsorption of Sr and Cs on sediments representative of INTEC alluvium and provide sufficient data to determine that their results are comparable to in situ alluvium conditions. Based on the ability to match the Hawkins and Short (1965) strontium and cesium adsorption experiments, we conclude that, except for cesium, the selectivity coefficients selected from Appelo and Postma are applicable to INTEC alluvial sediments.

#### **4. COMPARISON OF THE ION EXCHANGE MODEL TO MEASURED ALLUVIUM $K_d$ VALUES**

A second set of data that can be used to test the ion exchange model and the model parameterization was collected by the USGS and Idaho State University (Liszewski et al. 1998). In this study, samples of alluvium and sedimentary interbeds from wells USGS-121 and USGS-123 were tested for a wide range of physical properties and were used to determine strontium  $K_d$  values. Of interest for the source release model are the measurements made in surficial alluvium.

Well USGS-121 is just north of the INTEC facility and well USGS-123 is just south of the INTEC facility. Samples of alluvium were collected from a number intervals from land surface to 29 ft in well USGS-121 and from land surface to a depth of 26 ft in well USGS-123. A total of 21 samples were analyzed for  $K_d$  values. The top two or three intervals in each well consisted of finer-grained material than the deeper samples. This difference will be seen in the measured  $K_d$  values. The two wells tested are adjacent to INTEC and samples were collected from a range of depths in the alluvium. Therefore, we conclude that the samples are representative of alluvium at INTEC and are comparable to materials likely to be in the tank farm.

Samples for  $K_d$  measurements were sieved to remove the size fraction greater than 4.7 mm. The remaining material was crushed until all of the material passed through a 2-mm sieve. Grain size distributions were measured and reported, so that measured  $K_d$  values can be corrected for the mass of material removed. Freundlich isotherms were fit to the experimental data. However, the “n” parameter in the Freundlich equation for all samples was very close to one. Therefore, the Freundlich isotherms are essentially linear, and the Freundlich K can be interpreted as a  $K_d$  parameter. Sample depths, gravel fractions, and corrected  $K_d$  values for alluvium are shown in Table 11. The samples near the surface have  $K_d$  values significantly greater than samples collected from greater depths. This reflects a fine-grained layer of loess deposited on top of the alluvial gravels. Average values for the deeper samples are shown that do not include the near-surface material (italicized values in Table 11). In well USGS-121, the average  $K_d$  was 20 mL/g and in well USGS-123 the average  $K_d$  is 23 mL/g.

Unfortunately, one of the parameters that was not measured on these samples was the cation exchange capacity. Therefore, PHREEQC cannot be used to model these experiments to validate the cation exchange model. However, PHREEQC can be used in an inverse manner. Using the water chemistry used in the  $K_d$  experiments and the measured  $K_d$  value, PHREEQC can be used to calculate what the CEC of the sediments must have been to get the measured  $K_d$  value. This is not an independent verification of the cation exchange model because the CEC of the samples is not available. However, it will provide an estimate of the CEC of the samples, which can be compared to measured values of CEC from other studies.

Table 11. Measured  $K_d$  values from Liszewski et al. (1998).

Well USGS-121 Surficial Sediments				
Freundlich K	Freundlich n	% > 4.7 mm	Depth (ft)	Corrected $K_d$ (mL/g)
93	1.0	0.0	2.3	93
145	1.1	0.0	4.3	145
144	1.0	0.0	6.2	144
61	0.97	75.5	13.1	15
61	0.99	74.2	15.1	16
56	0.99	68.0	17.1	18
57	1.1	74.4	19.0	15
59	1.0	76.5	21.0	14
70	1.0	57.2	23.0	30
62	1.1	68.1	26.9	20
73	0.93	57.2	28.9	31
Average				20
112	1.1	36.8	2.0	71
52	0.89	59.7	4.3	21
40	0.92	55.7	5.9	18
48	1.1	54.7	9.8	22
48	1.1	69.6	12.1	15
57	0.84	66.0	14.1	19
61	1.1	62.4	16.1	23
58	0.92	50.0	18.0	29
85	0.96	54.6	21.0	39
70	1.3	65.2	25.6	24
Average				23



A plot of alluvium  $K_d$  values measured by Liszewski et al. (1998) against the CEC values calculated from the measurements using PHREEQC is shown in Figure 9. The correlation is perfect because there is a functional relation between the two variables, with no independent measurements. However, the calculated CEC values can be compared to measurements of CEC from alluvium. The calculated CEC values are shown in Table 12. The calculated CEC values range from 1.4 meq/100 g to 14.5 meq/100 g with an average of 3.9 meq/100 g. It is clear from the plot in Figure 9 that only a few values are greater than 5 meq/100 g. From the table, it is clear that these high CEC samples are associated with the near-surface fine-grained sediments, not the river alluvium. Therefore, from these calculations, the Liszewski et al. (1998) -measured  $K_d$  values are shown to be consistent with alluvium of the Big Lost River, having a narrow range in CEC values, and the range is between 1.5 meq/100 g and 4 meq/100 g. These numbers are very similar to the range of CEC values measured by the USGS in 1956.

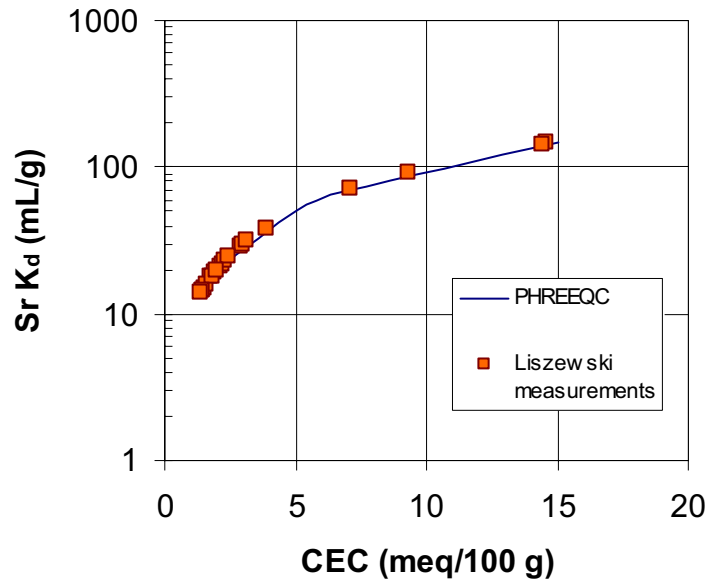


Figure 9. Plot of correlation between  $K_d$  values measured by Liszewski et al. (1998) and CEC values calculated from the measured  $K_d$  values using PHREEQC.

Table 12. CEC values for surficial alluvium calculated from measured  $K_d$  values in Liszewski et al. (1998).

Depth (ft)	Corrected $K_d$ (mL/g)	CEC (meq/100 g)
2.0	70.8	7.1
2.3	93.0	9.3
4.3	145.0	14.5
4.3	21.0	2.1
5.9	17.7	1.8
6.2	144.0	14.4
9.8	21.7	2.2
12.1	14.6	1.5

Table 12. (continued).

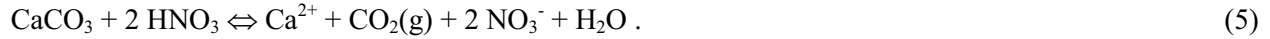
Depth (ft)	Corrected $K_d$ (mL/g)	CEC (meq/100 g)
13.1	14.9	1.5
14.1	19.4	1.9
15.1	15.7	1.6
16.1	22.9	2.3
17.1	17.9	1.8
18.0	29.0	2.9
19.0	14.6	1.5
21.0	13.9	1.4
21.0	38.6	3.9
23.0	30.0	3.0
25.6	24.4	2.4
26.9	19.8	2.0
28.9	31.2	3.1
Mean		3.9
Maximum		14.5
Minimum		1.4

## 5. ONE-DIMENSIONAL TRANSPORT SIMULATION

This section provides an overview of Sr-90 transport from the sodium-bearing waste release using a one-dimensional representation of the tank farm alluvium. The purpose of this section is to provide an overview of the relative transport rates of various dissolved species, changes in pH and mineral composition of the sediments, and a discussion of partitioning between sediment and pore water. This will provide a basic understanding of the processes that are taking place in the alluvium as the sodium-bearing waste is neutralized and migrates downwards. The sensitivity of the predicted Sr-90 migration to the natural background strontium concentration in the pore water is also evaluated. Quantitative analysis of the distribution of Sr-90 in the alluvium, calculation of the flux of Sr-90 from the alluvium to the underlying basalt, and analysis of the sensitivity to cation exchange capacity and selectivity coefficients are presented in Section 6. These analyses are based on a three-dimensional representation of the alluvium.

For the one-dimensional simulation, the leak and the alluvium are represented as a single column of alluvium with x and y dimensions of  $60 \times 30$  m ( $200 \times 100$  ft). The alluvium is divided into 36 cells each 0.5 m (1.64 ft) in height. Vertical locations in the alluvium are given as elevation above the basalt contact. To avoid problems with boundary conditions at the sediment – basalt interface, 10 cells were defined as basalt to allow the alluvium to drain freely. A constant vertical flux from infiltration was applied at the surface. Pore water, recharge, and sodium-bearing waste compositions are the same as for the three-dimensional model discussed below. A cation exchange capacity of 5 meq/100 g (midpoint of distribution in Figure 2) was used in the one-dimensional model.

In the first few steps of the computer simulation, the flux of water and the water content of the alluvium are allowed to come to steady state, resulting in a water saturation of about 30%. The leak was then simulated to occur in cell 33 (depth of 1.25 m), and the sodium-bearing waste was allowed to react with the alluvium and to be washed downwards by recharge from the surface. Acidic sodium-bearing waste reacts with calcite in the alluvium consuming hydrogen ion from the waste and releasing carbon dioxide:



While the sodium-bearing waste is neutralized by the calcite reaction, sufficient hydrogen ion remains to lower the pH of pore water. TOUGHREACT is a multiphase flow simulator, allowing the transport of  $\text{CO}_2$  as a gas and also as a constituent dissolved in water. Figure 10 shows the volume fraction of calcite in the alluvium 1 week and 1 year after the leak. One week corresponds to the maximum drop in pH in the release cell. The volume fraction of calcite is quickly reduced from the original quantity of 0.050 to 0.049 in the cell where the sodium-bearing waste was released. There is some additional dissolution of calcite in the release cell and in the cell immediately below the release point over the next year. The total amount of calcite dissolved is a small fraction of the total available calcite, so there should be adequate buffer capacity in the alluvium.

The pH of pore water in the release cell drops quickly, reaching a minimum value of 5.7 one week after release (Figure 11). The pH of the water moving downward from the cell where the leak occurred remains less than the initial pore water pH of 7.3 because of the increased  $\text{CO}_2$  partial pressure from calcite dissolution. The increased partial pressure of  $\text{CO}_2$  dissolves a small amount of calcite in the cells immediately below the release depth. The model indicates that the calcite in the alluvium rapidly buffers the pH of the sodium-bearing waste so that extreme pH values are not observed in the pore water. There will be a transient pH drop from the release of carbon dioxide from calcite dissolution, but this dissipates within a matter of weeks. The minimum pH of pore water after the initial calcite dissolution is about 6.5, and this pH-minimum moves down through the alluvium over a period of about 4 years. As the peak concentrations of the sodium-bearing waste move downward, the cation ratio in the pore water changes back to natural levels. Calcium in the recharge water replaces sodium from the ion exchange sites. As a result, the pore water becomes undersaturated with respect to calcite, and some calcite dissolves. The dissolution of calcite to replace the calcium lost to ion exchange sites raises the pH in the pore water to about 7.5. Once the excess sodium has been replaced by calcium on the ion exchange sites, the pore water pH will return to about 7.3.

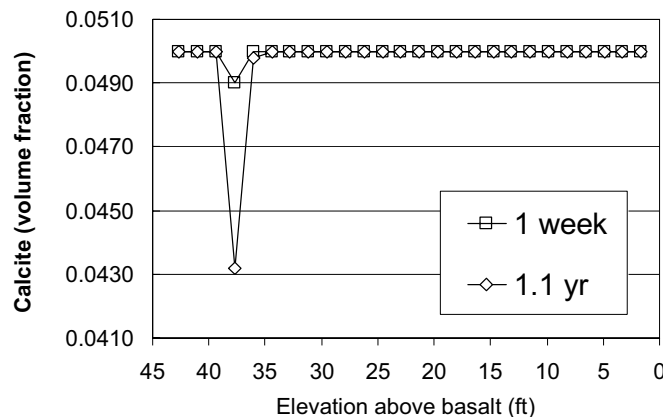


Figure 10. Volume fraction of calcite at 1 week and 1 year after release of sodium-bearing waste.

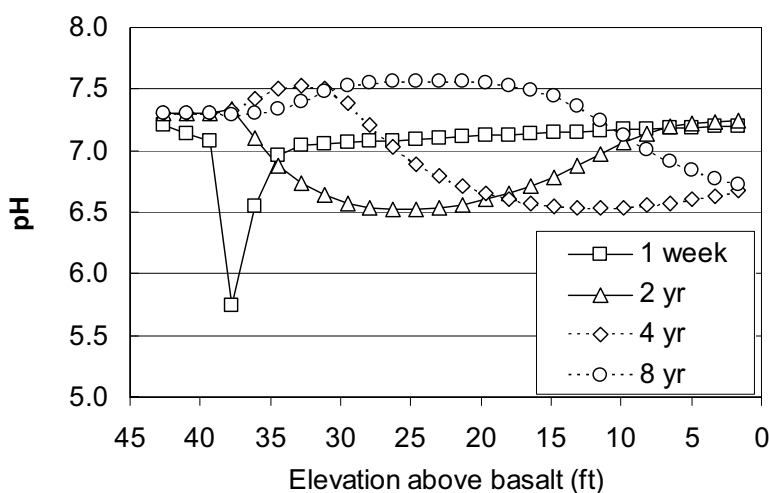


Figure 11. Vertical profiles in alluvium pore-water pH.

In the immediate vicinity of the release, 0.0012 volume fraction of gibbsite is formed as the sodium-bearing waste is neutralized (not shown). This small amount will not affect hydraulic properties of the media. Because the lowest pH predicted by the model is 5.7, the amount of dissolution of aluminosilicate minerals, such as feldspars, will be relatively minor and does not need to be included in the model.

The mobility of the major ionic species will depend on reactions with ion exchange sites on the clay minerals. Cations will react with ion exchange sites, and may migrate slower than nitrate, which is considered a conservative species. The distribution of major dissolved species after 2.03 years is shown in Figure 12. Peak nitrate concentrations have been reduced from 4.5 M to 0.4 M by mixing with pore water in the alluvium. Nitrate and calcium have migrated the farthest and move at about the same rate as indicated by the coincident rise in concentrations of both components between elevations above the basalt interface of 10 to 20 ft. Nitrate is from the sodium-bearing waste, and calcium is generated by the dissolution of calcite by nitric acid. Because calcium is essentially saturated on exchange sites in the alluvium, there is little loss by ion exchange and no discernable retardation. Sodium, on the other hand, is significantly retarded relative to nitrate and calcium. Most of the ion exchange sites in the alluvium are initially filled with calcium, so the high sodium concentrations in the sodium-bearing waste drive exchange reactions where sodium knocks calcium off the clays. Calcium, therefore, is kept in solution, but some of the sodium is removed.

Initial concentrations of Sr in the sodium-bearing waste are on the order of  $2 \times 10^{-5}$  M. At 2 years, there is a strontium peak migrating at about the same rate as the peaks in major cations, and showing similar retardation as sodium relative to the migration of calcium (Figure 13). The retardation of strontium relative to calcium indicates that strontium does interact with ion exchange sites on the clays. Two factors however, inhibit strontium adsorption, which keeps more strontium in solution than would be predicted by a constant  $K_d$  model. One factor is the competition for ion exchange sites, and the second factor is the formation of aqueous complexes of strontium in solution.

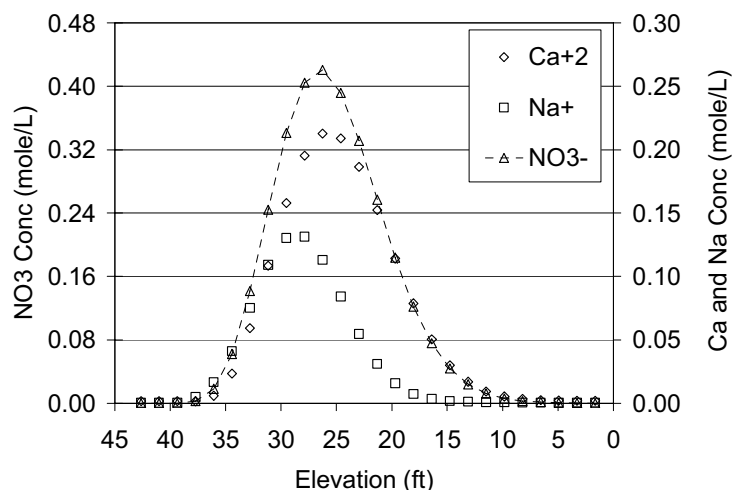


Figure 12. Distribution of calcium, sodium, and nitrate in pore water with depth in the alluvium 2.03 years after the leak.

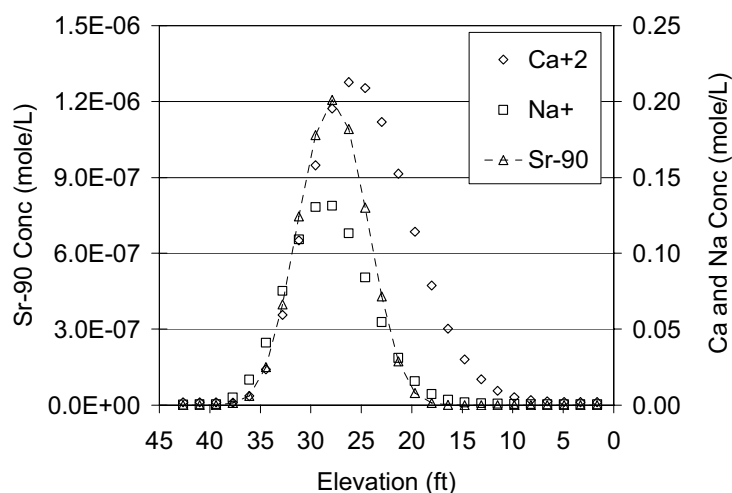


Figure 13. Distribution of strontium, sodium, and calcium in pore water with depth in the alluvium 2.03 years after the leak.

The distribution of strontium between aqueous species and ion exchange sites shows significant variations with depth that are correlated to the peaks in the major chemical components in the sodium-bearing waste (Figure 14). In normal pore water, 98.6% of the strontium is on exchange sites, and only 1.4% in solution. In the sodium-bearing waste solution, however, only about 30% of the strontium is on the ion exchange sites and 70% in aqueous solution. This partitioning to the aqueous phase is responsible for the more rapid migration of strontium. Two factors decrease strontium partitioning to clays. The first factor is the formation of soluble aqueous complexes of strontium with nitrate ion. About 24% of the strontium is in the form of aqueous nitrate complexes, and, therefore, is sequestered in solution and will not adsorb as strongly on clays (Figure 14). There is also a decrease in partitioning of strontium ion ( $\text{Sr}^{2+}$ ) to clays with free strontium in solution increasing from 1.4% to 44%. The decrease in partitioning is the result of increased competition for ion exchange sites by elevated calcium and sodium concentrations in solution. Both competitive cation exchange and formation of aqueous complexes are needed to accurately predict the transport of strontium from the sodium-bearing waste leak.

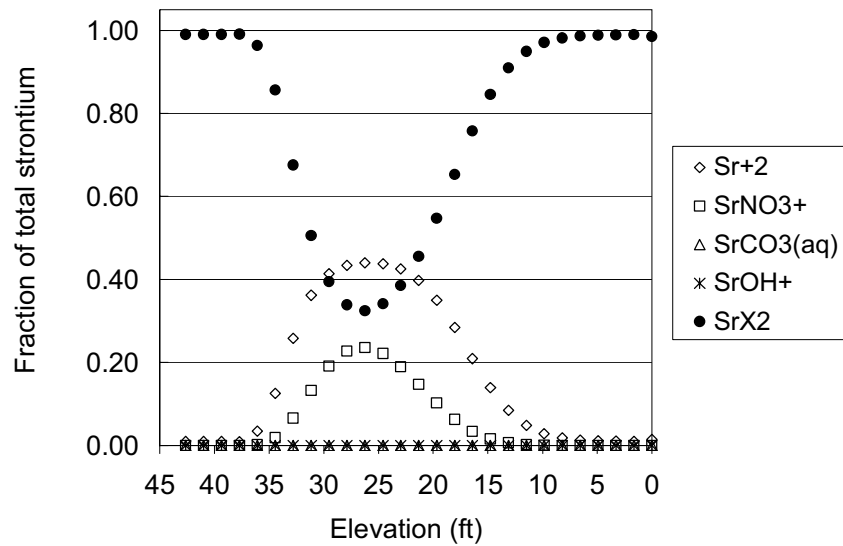


Figure 14. Distribution of strontium among aqueous species and ion exchange sites at 2.03 years after release.

The replacement of calcium on ion exchange sites by sodium is well illustrated in Figure 15, where the concentrations of the exchangeable cation species are shown. The exchangeable calcium concentration is at a minimum where the sodium maximum is located at an elevation of about 30 ft 2.03 years after the release. As the sodium peak migrates downwards through the alluvium, some of the strontium is left behind on ion exchange sites (Figure 15 B, between 35 and 40 ft elevation). Thus, the elevated cation concentrations from the sodium-bearing waste spill enhance the transport of the strontium through the alluvium. However, once those peak concentrations have migrated downwards, the preferential partitioning of strontium over calcium to cation exchange sites results in a much less mobile fraction of strontium. Also, the decrease in nitrate concentration decreases the formation of soluble aqueous complexes of strontium.

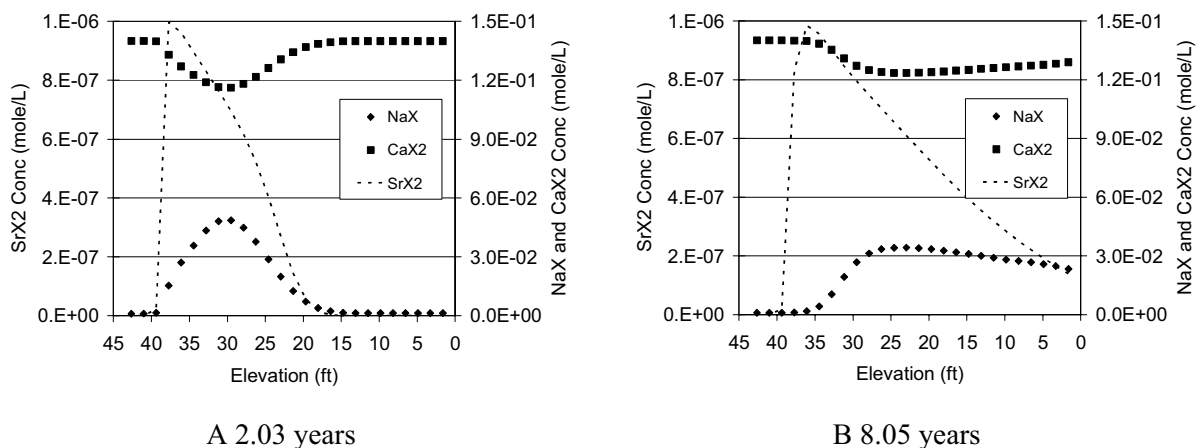


Figure 15. Distribution of exchangeable cations with depth in the alluvium 2.03 (A) and 8.05 (B) years after the leak.

The elevated aqueous strontium concentration near the sediment - basalt interface (elevation 0 ft) at 8.05 years (Figure 16) is not matched by an elevated concentration of strontium on ion exchange sites at the corresponding time and elevation (Figure 15 B). However, the elevated aqueous concentrations of strontium at 8.05 years at an elevation of 35 to 40 ft does correspond to an elevated concentration on exchange sites where the aqueous sodium and calcium concentrations have returned to near normal levels. Translating this information into a time history of release for strontium-90 (Figure 17) shows that there will be about a two-order-of-magnitude higher release of strontium-90 because of the competition of exchange sites from sodium and calcium. Peak releases from the alluvium to the underlying basalt are calculated (in the one-dimensional model) to take place between about 4 and 12 years after release. Once the cation peak has passed, there will be a steady release of strontium, which is similar to what would be predicted with a  $K_d$  model.

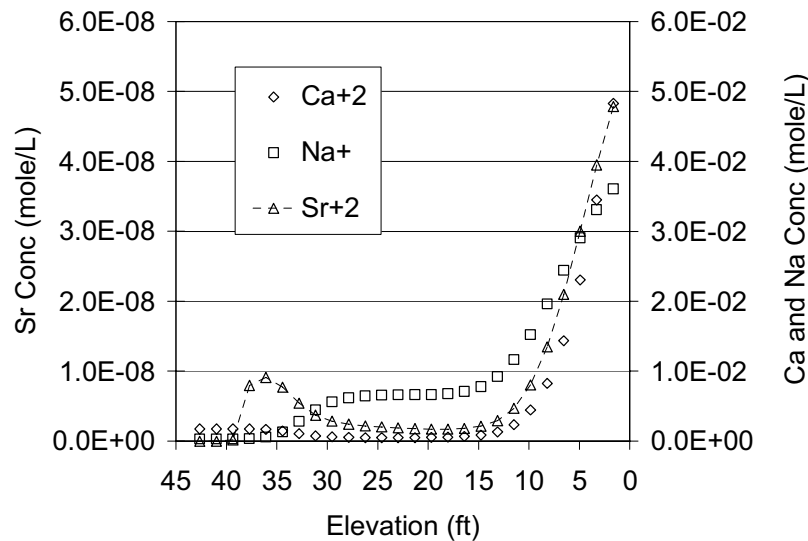


Figure 16. Concentration of cations in solution at 8.05 years.

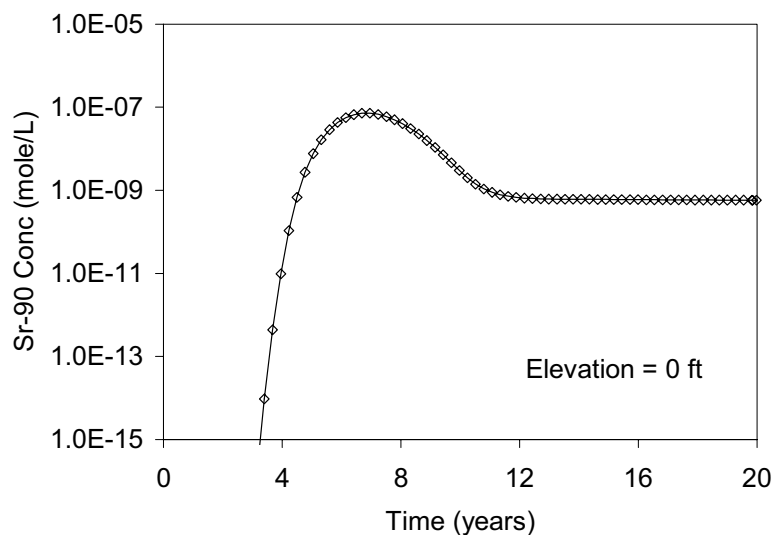


Figure 17. Concentration of Sr-90 in pore water at the sediment-basalt interface.

Two factors enhance the transport of strontium through alluvium immediately after the leak. Some strontium forms complexes with nitrate at the very high concentrations in the sodium-bearing waste and is prevented from sorbing to clays. In addition, high sodium and calcium concentrations inhibit the sorption of strontium to ion exchange sites. After 8.05 years (Figure 16), there is a peak of strontium migrating downwards in conjunction with the peak concentrations in sodium, calcium, and nitrate. The initial breakthrough fronts of nitrate and calcium move more rapidly because these two species are not retarded (Figure 12). Significant strontium remains on ion exchange sites behind the sodium peak, and there is a continuous slow release of strontium from these exchange sites. Including the high ion concentrations from the sodium-bearing waste leak results in a variable partitioning of strontium to the ion exchange sites from aqueous complexation and competitive ion exchange.

The changes in partitioning with depth corresponding to changes in the bulk water chemistry can be illustrated by calculating a local effective  $K_d$  value at each depth. This is calculated from the predicted sorbed concentration and the predicted aqueous concentration by:

$$K_d = \frac{C_{ads}}{C_{sol}} \cdot \frac{S_l \cdot \theta}{\rho} \quad (6)$$

where

- $C_{ads}$  = adsorbed concentration (mol/L)
- $C_{sol}$  = dissolved concentration (mol/L)
- $S_l$  = saturation ( $\text{cm}^3$  of water/ $\text{cm}^3$  of rock)
- $\theta$  = porosity ( $0.32 \text{ cm}^3/\text{cm}^3$ )
- $\rho$  = bulk density ( $1.8 \text{ g rock}/\text{cm}^3$  of rock).

Using Equation (6) and the parameter values given with it, predicted solid and aqueous concentrations of strontium can be used to calculate  $K_d$  values. These values are shown in Figure 18 for 1.2, 8, and 20 years after the leak. In the native pore water, the strontium  $K_d$  is predicted to be about 6 mL/g at a water saturation of 0.32. Adjusting this  $K_d$  to water saturation involves multiplying by a factor of 3 ( $1/0.32$ ), giving a saturated  $K_d$  of about 18 mL/g. During the leak, when calcium and sodium concentrations in pore water are at their peak values, strontium  $K_d$  values can drop to about 0.02 mL/g. As the water moves downward through the alluvium and mixes with native pore water, peak concentrations of sodium and calcium decrease, resulting in an increase in  $K_d$  values for strontium (Figure 18). By 20 years, effects of the sodium-bearing waste leak are almost gone, and partitioning of strontium has returned to normal.

One side effect of linking of  $K_d$  to solution concentrations is that there will be a bimodal transport of strontium through the vadose zone. Strontium traveling with the sodium peak will move faster than strontium that falls behind the sodium peak (see Figure 16). Thus, some strontium could move downward out of the alluvium relatively rapidly. Strontium remaining in the alluvium would migrate very slowly, because the pore water chemistry would have changed substantially.



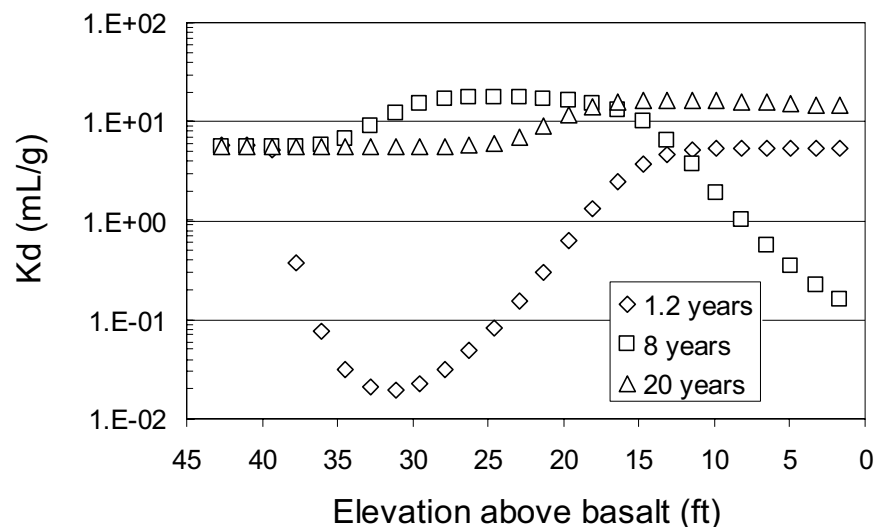


Figure 18. Distribution of strontium between aqueous and solid phases with depth between 1.2 years, 8 years, and 20 years after the leak.

## 5.1 Presence of Stable Strontium

Pore water in the alluvium will have stable strontium. This strontium will also compete for ion exchange sites and will have the same selectivity as radioactive Sr-90. Therefore, this strontium may have an effect on the partitioning of Sr-90. The effect of stable strontium was evaluated using the one-dimensional transport model. Calculations were performed after adding a second strontium species to the TOUGHREACT database with exactly the same chemical properties as radioactive Sr-90. The concentration of stable strontium was selected as 0.007 mmol/L (Table 4). This is the highest concentration measured in perched water wells by Roddy (2005) and will give the highest likely amount of competition for exchange sites in alluvium.

The peak strontium-90 concentration at the sediment-basalt interface (Figure 19) occurs 7 years after the leak. Without stable strontium in the system, the peak concentration is predicted to be  $7.183\text{E-}08$  mole/L. With 0.007 mmol/L stable strontium, the peak release concentration increases to  $7.196\text{E-}08$  mole/L, or a change of 0.18%. Based on this comparison, the inclusion of stable strontium does not make a significant change in the predicted release of Sr-90 from the alluvium. Therefore, stable strontium was not included in the three-dimensional simulations to decrease the size of the chemical matrix that needed to be solved.

Based on this analysis, the ion exchange model adequately represents the chemical evolution of the CPP-31 release. This one-dimensional analysis is useful in developing an understanding of initial rapid transport of strontium through the alluvium and into the underlying basalt followed by a slow-delayed release of strontium from the alluvium under pseudo-static geochemical conditions. Evaluation of the site-specific applicability requires comparison of known field data to geochemical model predictions and an analysis of the predictive sensitivity to model parameter uncertainty. The site-specific application is presented in Section 6.

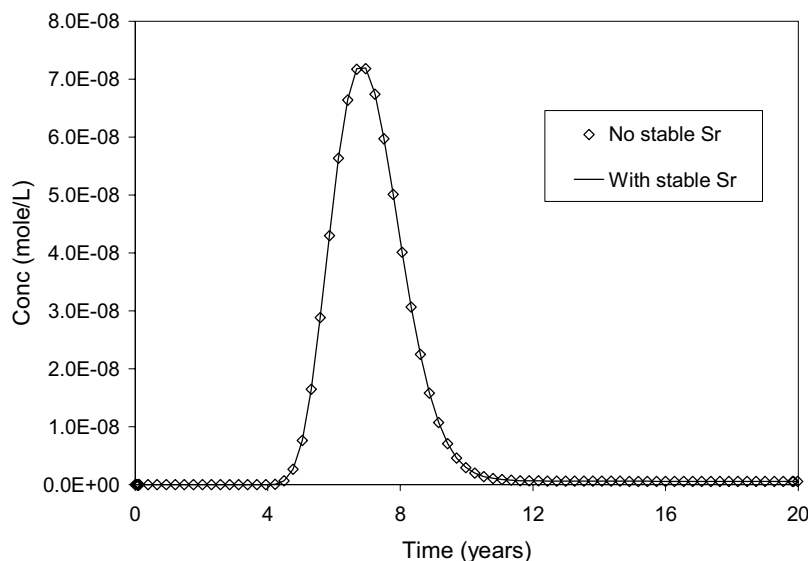


Figure 19. Simulated Sr-90 concentrations at the sediment – basalt interface comparing cases that include or do not include natural, stable strontium at a concentration of 0.007 mmolar.

## 6. SITE-SPECIFIC APPLICATION AND DETERMINATION OF MODEL SENSITIVITY

Evaluation of the model applicability and data sufficiency to the CPP-31 release was performed as a three-step process. In the first step, site-specific field data were compiled for use in direct model to data comparison. In the second step, the one-dimensional model was reconfigured into a three-dimensional system more representative of the physical conditions during the CPP-31 release. The three-dimensional model was then run, and model predictions were compared to the field data. The third step analyzed the overall model sensitivity to input parameters. This final step is necessary to evaluate whether the available data are sufficient to draw conclusions about strontium risk from the alluvium. It involves determination of the sensitivity of predicted results to uncertainty in the input parameters. Even if parameters are poorly constrained, if the final result is relatively insensitive to the parameter, collecting additional data to reduce uncertainty may not be justified. In this last section, sensitivity to three factors is considered:

(1) uncertainty in the cation exchange capacity, (2) uncertainty in the selectivity coefficient for strontium, and (3) uncertainty to pore water chemistry.

### 6.1 Site-Specific Configuration for CPP-31

The base model used in this analysis is a three-dimensional representation of the CPP-31 release. Beginning with the previously parameterized one-dimensional hydrogeochemical model, the short-dimension in the horizontal plane (Y-direction) was subdivided into five grid blocks each 6 m in extent. This results in a final discretization of  $20 \times 5 \times 36$  blocks over a volumetric extent of  $60 \times 30 \times 18$  meters oriented in the x-y-z directions. Under the release location, a low-permeability, low-porosity, geochemically inert barrier was placed at a depth of 5 m. This barrier represents the plumbing conduit that underlies the CPP-31 release location. It is thought that the released fluid flowed along this barrier and was distributed horizontally under capillary and dispersive forces prior to being transmitted vertically through the alluvium. The barrier is represented by one grid block in both the Y- and Z- directions and extends most of the way across the X-direction. In an attempt to reproduce as

much of the actual hydrologic condition present at the time of release, the leak was simulated to occur over a period of 5 days and was initially released in a single grid block. The released liquid flowed across the top of the barrier and leaked over the edges into the next two adjacent grid blocks in the horizontal plane. After only 50 days, the water saturation in the vicinity of the barrier stabilized, achieving pseudo-steady state with respect to water potential and saturation. When the leak chemistry was included in this initial simulation, the numerical solution became unstable, and chemical mass balance was lost. The loss of mass balance is a function of the manner in which TOUGHREACT accounts for liquid volume in each cell as the saturation changes in time. To achieve numerical stability, the sodium-bearing waste was released in the model over a time period of 50 days (rather than 5 days). Because the resulting saturation profiles are similar at the end of the 50 days, it is felt that this modification is insignificant.

The model was then run for a 20-year period to obtain cesium and strontium concentrations.

## 6.2 Sensitivity to Geochemical Inputs

Sensitivity to the cation exchange capacity and selectivity coefficients were determined through simulation using the base model discussed in Section 5.1. In these sensitivity simulations, a single parameter change was made. The base simulation assumed a CEC of 7 meq/100 g, a strontium selectivity coefficient of 0.35, and a background sodium concentration of 3.3 mmol/L. The sensitivity to cation exchange capacity includes simulations using a CEC of 2 meq/100 g, 5 meq/100 g, 7 meq/100 g, or 15 meq/100 g. The sensitivity to strontium selectivity coefficient ( $K_{Na/Sr}$ ) used a range from 0.25 to 0.45. Sensitivity to background sodium concentration evaluated the effect of lowering pore water sodium concentrations to 0.22 mmol/L. To assess model sensitivity, we have chosen to look at (1) total activity leaving the alluvium at periods of 5, 10, 15, and 20 years and (2) effective adsorption capacity ( $K_d$ ) after 20 years. These results are presented in Table 13.

Table 13. Results of sensitivity simulations to evaluate the effect of parameter uncertainty. All Sr-90 activities are undecayed.

Performance Measure	Parameter						
Activity Leaving Alluvium (years after release)	CEC=7 <sup>a</sup> (meq/100 g)	CEC=15 (meq/100 g)	CEC=5 (meq/100 g)	CEC=2 (meq/100 g)	$K_{Na/Sr}=0.25$	$K_{Na/Sr}=0.45$	$Na^+ = 0.22$ mmol/L
5	1,773	349	2,793	5,187	1,658	3,090	1,921
10	6,378	1,715	8,352	12,272	3,369	9,454	6,497
15	6,393	1,725	8,368	12,310	3,373	9,470	6,509
20	6,403	1,731	8,380	12,336	3,378	9,480	6,517
$K_d$ range (mL/g) (at 20 yr)	7–30	20–50	4–18	1.5–4	15–50	7–15	10–35

a. Base case: CEC = 7 meq/100 g;  $Na^+ = 0.33$  mmol/L;  $K_{Na/Sr} = 0.35$ .

In the model, 15,000 Ci of Sr-90 were released to the alluvium by the leak. From the one-dimensional model, we saw that a fraction of the strontium moves relatively rapidly through the alluvium either complexed with nitrate ion or because of inhibition of adsorption as a result of competition with elevated sodium and calcium concentrations in solution. Once the sodium-bearing waste peak has passed through the alluvium, the remaining strontium on the ion exchange sites is released much more slowly. With the parameters used in the model, the sodium-bearing waste pulse leaves the alluvium between 5 and 10 years after release. Therefore, we see some fraction of the 15,000 Ci released within the first 10 years, with only a small incremental increase at 20 years (Table 13).

In the base case, 6,378 Ci of Sr-90 are released at 10 years. As the CEC decreases from 5 to 2 meq/100 g, the amount of Sr-90 released increases significantly from 8,352 Ci for 5 meq/100 g to 12,272 Ci for 2 meq/100 g at 10 years. Increasing the CEC to 15 meq/100 g has the opposite effect and decreases the amount of Sr-90 released at 10 years to 1,715 Ci. From the simulated partitioning of strontium between liquid and solid phases we can calculate  $K_d$  values (see Equation (6) in Section 4) for the alluvium. There is quite a range in calculated partitioning coefficients (Table 13). For CEC of 2 meq/100 g,  $K_d$  values are much lower than commonly considered applicable to alluvium. For higher CEC values, however, the ranges of calculated  $K_d$  values are comparable to values used previously in models and measured in alluvium. Even the  $K_d$  values at 15 meq/100 g are comparable to  $K_d$  values measured by the USGS (Liszewski et al. 1997, 1998).

All the CEC values used in the sensitivity runs are within the range of data obtained from the literature for INTEC alluvium. Changing the CEC produces two changes in model output. First, the fraction of the total Sr-90 released in the first 10 years is affected. Second, the steady-state  $K_d$  value after the leak has been flushed from the alluvium is affected. Decreasing the CEC results in more Sr-90 being flushed quickly from the alluvium. It also results in the remaining Sr-90 being more mobile. Higher CEC results in more Sr-90 being retained in the alluvium. However, the steady-state  $K_d$  value is higher so that this residual Sr-90 will be less mobile. The amount of residual Sr-90 and the mobility of the residual Sr-90 are important for evaluating risk and remedial alternatives. The amount of Sr-90 released from the alluvium in the first 10 years will affect perched water concentrations and may impact the selection of parameters for the vadose zone model to match measured Sr-90 concentrations in perched water.

The chemical composition of the pore water was estimated from measurements taken in perched water zones (Table 4). These measurements reflect multiple sources of water, some of which contain contaminants or dissolved solids from plant water systems. Recharge in the alluvium is likely to be closer in composition to precipitation and may have lower concentrations of sodium. Because sodium is one of the cations important in the competitive cation exchange reactions, the sensitivity of strontium transport to a lower sodium concentration in pore water/recharge was assessed. The other components in pore water are based on the assumption of calcite saturation at a partial pressure of carbon dioxide of  $10^{-2}$  atm. This assumption fixes carbonate, pH, and calcium within a fairly narrow range. Therefore, there is a limited range in uncertainty for calcium and pH and sensitivity to these parameters was not tested.

The sodium concentration used in the pore water model is the lowest measured in perched water and is equal to the concentration of sodium in the Snake River Plain Aquifer. Precipitation may have a lower concentration. Sensitivity to sodium concentration was tested by dropping the sodium concentration to 0.22 mmol/L from 0.33 mmol/L in the base case. The change in sodium concentration resulted in a very slight increase in the release of Sr-90 at 10 years (Table 13). The likely reason for this is that the lower background sodium concentrations increase the calcium saturation on the ion exchange sites. The greater fraction of calcium on the clays decreases the partitioning of strontium to ion exchange sites. This decrease is small and does not increase the release of Sr-90 significantly. Therefore, the Sr-90 release is not sensitive to background concentrations of sodium in the pore water, and the estimated values used in the model do not need to be refined.

The third parameter evaluated for effect on Sr-90 release is the strontium selectivity coefficient. The selectivity coefficient is primarily related to the properties of the cation. Cations in solution are not equally sorbed to ion exchange sites on clays. Cations with greater hydrated ionic potential are preferentially sorbed. This means that divalent cations are more strongly bound than monovalent cations. Larger cations (greater atomic number) in a group are less strongly hydrated than smaller cations. As a result of the lower hydration, cations with greater atomic number have fewer waters of hydration and, consequently, a greater hydrated ionic potential. Thus, the order of preference for divalent alkaline earth

cations is  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ . Strontium will be more strongly sorbed to ion exchange sites than calcium and magnesium, as well as the monovalent cation sodium.

The selectivity coefficient of strontium was varied to be as low as calcium and as high as barium. Given the general consensus on the ordering of selectivity coefficients, this effectively brackets the total range over which the selectivity coefficient could range. The selectivity of strontium was lowered to a value (0.45) slightly lower than calcium. This increased the release of Sr-90 to 9,454 Ci because calcium and sodium were much more effective at competing for exchange sites with strontium. Raising the selectivity coefficient to a value more representative of barium decreased the release of Sr-90 to 3,369 Ci at 10 years. The calculated release of Sr-90 is sensitive to the selectivity coefficient for strontium. The range of selectivity coefficients tested exceeds the likely range in uncertainty in the selectivity coefficient because, if the values selected were true, it would alter the selectivity sequence for cations. Furthermore, the selectivity coefficients used in the base case do a good job of matching laboratory measurements of strontium sorption to INTEC sediments. Therefore, we conclude that additional refinement of selectivity coefficients for INTEC-specific materials is not likely to significantly impact the uncertainty in the calculated Sr-90 release from alluvium.

## **7. CONCLUSIONS AND RECOMMENDATIONS**

Sodium-bearing waste released to the tank farm alluvium in 1972 was very acidic; contained high concentrations of sodium, aluminum, and nitrate; and contained 15,000 Ci of Sr-90. Because of the highly dynamic geochemical evolution of pore water chemistry as the released sodium-bearing waste migrated through the tank farm alluvium, a competitive cation exchange model was evaluated as a method to provide better estimates of Sr-90 migration. The purpose of this report is to evaluate existing data that could be used in a competitive cation exchange model of Sr-90 transport in the tank farm alluvium. These data are evaluated to determine if sufficient data of suitable quality currently exist to provide a defensible simulation of Sr-90 transport. Data evaluation included

- Number and spatial distribution of cation exchange capacity measurements
- Selectivity coefficients for competitive ion exchange of strontium
- Sensitivity of the reactive transport model to the measured range of CEC
- Sensitivity of the reactive transport model to uncertainty in the strontium selectivity coefficient.

Based on an evaluation of these factors, the need for additional data on CEC or selectivity coefficients was determined.

### **7.1 Mineral Data**

Large amounts of data exist on mineralogy and grain-size distribution of INTEC alluvium. Sufficient data exist to conclude that calcite will be present at about 5 vol% in the alluvium to neutralize the acid. The simulations show that there is a large excess of calcium over the amount needed to buffer the sodium-bearing waste, so the simulations will not be sensitive to significant changes in this number.

Quite a few analyses of cation exchange capacity are representative of alluvium at INTEC. Samples analyzed for CEC by the USGS in 1956 and by DOE in 1965 are either representative of in situ alluvium or are supported by sufficient data to permit adjustment of the CEC values to be representative of alluvium. These samples came from a number of locations around INTEC and from a range of depths

within the alluvium. The range of CEC values from these two data sets is relatively small, 2 to 4.5 meq/100 g with a mean of 3 meq/100 g. An estimated correction factor was used to adjust the ecological risk assessment CEC values. There is significantly more uncertainty in these data, but the range of values after adjustment is from 2 to 8 meq/100 g. CEC values for alluvium were calculated from strontium  $K_d$  values measured by Liszewski et al. (1998) using the cation exchange model in PHREEQC. A few samples of fine-grained near-surface sediments gave high CEC values. Calculated CEC values for gravel alluvium ranged from 1.4 to 3.9 meq/100 g. New samples collected from alluvium are not likely to yield CEC values that fall outside this range of values. Therefore, additional CEC data are not likely to decrease the uncertainty in the estimated range of Sr-90 released from the alluvium.

## **7.2 Selectivity Data**

Good agreement on the order of selectivity preference for cations for a wide range of materials presented by a number of authors indicates that selectivity coefficients should vary over a fairly narrow range and be primarily controlled by the identity of the cation, not by the sedimentary materials. No site-specific selectivity coefficients have been measured on INL Site or INTEC materials.

Laboratory data collected by Hawkins and Short in 1965 provide data from a series of sorption experiments that can be used to evaluate the ion exchange model for INTEC sediments. Sorption of Sr to INTEC alluvium is well explained by ion exchange on planar surfaces of clay minerals using selectivity coefficients from the literature. Sorption of Cs is more complex and occurs to a greater extent than predicted by literature selectivity coefficients. Cs sorption requires two ion exchange sites. A planar ion exchange site and a very strong ion exchange site, probably associated with the frayed-edges of clay minerals, are present at very small amounts. For trace amounts of radionuclides, however, these strong ion exchange sites are sufficient to accommodate most or all of the radiocesium in the sodium-bearing waste.

Based on the concurrence in the literature on the order of selectivity preference of cations for ion exchange and the ability of the selectivity coefficients adopted from the literature to match the laboratory experiments of Hawkins and Short, we conclude that refinement of the selectivity coefficients is not justified.

## **7.3 Recommendations**

The competitive cation exchange geochemical model of Sr-90 transport coupled with low CEC values for INTEC alluvium predict that between 6,000 and 12,000 Ci of Sr-90 may have been released from alluvium during the first 5 years after the leak. The competitive cation exchange model incorporates processes that affect the partitioning of Sr to soil minerals, including competitive cation exchange, pH, complexing with ligands in solution, and dissolution of calcite. Because of this, the estimate of initial Sr-90 transport is much more defensible and accurate than previous estimates based on fixed partitioning ( $K_d$ ) coefficients. While some uncertainty remains concerning the CEC in alluvium, the range in uncertainty is relatively small, and additional sampling is likely to support a CEC within this range. Therefore, we do not recommend sampling of alluvium for additional CEC determination.

We recommend that the ion exchange selectivity coefficients determined from fitting the Hawkins and Short data be used in the OU 3-14 geochemical model. The range over which the strontium selectivity coefficient can vary is constrained by the coefficients of calcium and barium. Within that range, the results are much less sensitive to the strontium selectivity coefficient than to CEC. Also, these coefficients match site-specific ion exchange experiments conducted on Big Lost River alluvium.

The competitive cation exchange model shows that partitioning of strontium between pore water and sediment varies considerably because of the chemistry of the sodium-bearing waste. Complexing of strontium with nitrate and competition for cation exchange sites significantly affects Sr-90 partitioning. Taking the simulated partitioning and calculating effective  $K_d$  values show that the  $K_d$  changes from about 6 mL/100 g to as little as 0.02 mL/100 g in the sodium-bearing waste plume. This demonstrates that a single  $K_d$  approach cannot capture very important changes in the mobility of strontium while the sodium-bearing waste peak is leached from the alluvium. We recommend that the TOUGHREACT reactive transport model be used to simulate the source term in the alluvium during initial waste release and that the Sr-90 fluxes be used as input to the TETRAD modeling of the deeper vadose zone.

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